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BREWING
SCIENCE AND PRACTICE

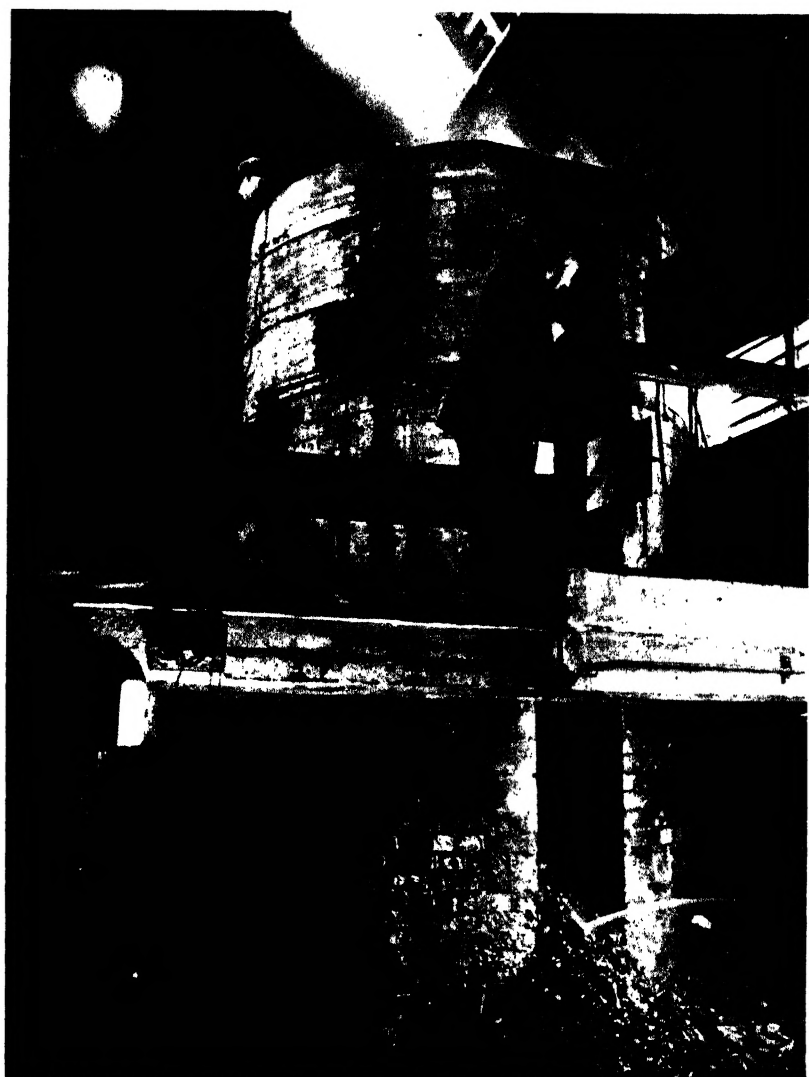


Photo: K. Hubschmann, London

FIG. 1

THE QUEEN'S COLLEGE BREWERY, OXFORD
THE COPPER

Frontispiece

BREWING

SCIENCE AND PRACTICE

By

H. LLOYD HIND

B.Sc., F.R.I.C., F.R.M.S.

VOLUME I

BREWING PROCESSES

THIRD IMPRESSION



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AUTHOR'S PREFACE

THE author hopes that this book on brewing will be found of use both by brewers and those engaged in the scientific side of brewing. He has been more than ever impressed during its preparation by the wide additions to pure scientific knowledge that have originated in the endeavour to elucidate the mysteries of brewing and, perhaps equally, by realisation of the inadequacy of our present interpretation of many of them. A quotation from Marshal Saxe's "Reveries on the Art of War," written in 1750, must have applied with equal force in his day to brewing and it can hardly be said to have lost all its point to-day. "It is a science so obscure and imperfect that custom and prejudice, confirmed by ignorance, are its sole foundations and support, with sacrosanct dogmas no better than maxims blindly adopted without any examination of the principles on which they were founded."

All this applied to brewing in the eighteenth century, but, with the nineteenth, came an increasing urge to discover those principles. This spirit of investigation has spread among brewers, with constantly increasing force to the present day. Brewing is an art, not a science, and it would be presumptuous to attempt to teach it in any other way than by actual demonstration, but no artist is content to work in the dark to rules laid down by his predecessors. He seeks the guidance of the underlying scientific principles, and studies the hypotheses woven round them in attempts to explain the why and wherefore, with constant hope that some of them may prove helpful in practice. The position may again be illustrated by a quotation from Hilaire Belloc's translation of *Des Principes de la Guerre*. Marshal Foch opened his book by asking whether war could be taught, and his answer applies equally well to brewing. The results of his study of history were a *theory* that could be taught and a *doctrine* that must be practised. "What is meant by these words is the conception and practical application, not of a science of war nor of some limited dogma, composed of abstract truths outside which all would be heresy, but of a certain number of principles, the application of which, though they will not be open to discussion once they shall have been established, must logically vary according to circumstances, while always tending towards the same goal, and that an objective goal."

AUTHOR'S PREFACE

It is extremely difficult adequately to survey and to present in an intelligible manner the results of modern enquiries into the scientific principles of brewing. They cover such an immense field of research, that it is difficult to grasp them all and focus the discoveries of specialists in so many branches of science on to their practical application or to give a balanced view of theories, any one of which may appear to its originator as the panacea for many difficulties. The attempt to do this has involved reference to the work of a very large number of investigators, and that so many are devoting their activities to the more scientific aspects of brewing should be a source of satisfaction to an industry that has, for so long, prided itself on its contributions to scientific advance. Students demand details of the evidence on which modern theories are based, and this has required reference to original sources, wherever possible. Since these are scattered in Journals in so many languages, it has been thought desirable to add references to the abstracts in the Journal of the Institute of Brewing.

It would have been impossible to produce this book without the help given so ungrudgingly by friends engaged in scientific investigation and in the practice of brewing or its allied industries. The author offers them all his most grateful thanks and, if it is not invidious to mention two names, it would be those of Dr. L. R. Bishop and Professor R. H. Hopkins.

H. LLOYD HIND.

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PUBLISHERS' NOTE

It is with the deepest regret that we have to issue posthumously this reprint of Mr. H. Lloyd Hind's classic work. We share with his innumerable friends in the brewing industry a sense of deep personal loss and a full appreciation of all that his untimely death means to the science which he did so much to advance.

The author's corrections to the first edition have been most ably embodied and supplemented by Mr. E. N. Hamnett, whom we thank most cordially for his courteous assistance in this and other directions. Without his valuable help the publication of the revised impression must have been considerably delayed.

CHAPMAN & HALL LTD.

CONTENTS

CHAPTER		SECTION
I.	HISTORICAL - - - - -	1

An Ancient Brewery—Theoretical Speculation—Fermentation—The Advance of Chemistry—Ferments—The Nature of Yeast—Pasteur—The Modern Era—Barley as the Raw Material of Brewing.

BARLEY

II.	THE STRUCTURE AND CLASSIFICATION OF BARLEY	10
-----	--	----

STRUCTURAL CHARACTERS OF BARLEY

The Ear of Barley—Wide-eared and Narrow-eared Barleys—The Barley Corn—Identification of Threshed Barleys—Development of the Barley Corn—Microscopic Structure of the Barley Corn.

CLASSIFICATION OF BARLEYS

Species and Races—Classification—Summary.

III.	MALTING BARLEYS - - - - -	19
------	---------------------------	----

BRITISH BARLEYS

Older Varieties—Selection and Hybridisation—Plumage-Archer and Wide-eared Barleys—Spratt-Archer and Narrow-eared Races—Barley Types and Districts—Varietal Characteristics.

FOREIGN TWO-ROWED BARLEYS

German and Czecho-Slovakian Barleys (Hanna Strains)—Scandinavian Barleys—Other two-rowed Barleys.

SIX-ROWED BARLEYS

Mediterranean and Manchuria Types—Characteristics of Six-rowed Barleys—American Brewing Barleys—Manchuria and Oderbrucker Barleys—Smooth-awned Barleys—Californian Barleys—Mariout Barleys—Grading of American Malting Barley—No. 1 Standard Californian Barley—Canadian Barley Grades—Other Six-rowed Barleys—Types of Barley and Brewing Requirements—Summary.

CONTENTS

CHAPTER

SECTION

IV. PHYSIOLOGICAL CHARACTERS OF BARLEY - - 41

BARLEY QUALITY

Malting Quality—Ripeness and Maturity—Mealy and Steely Barleys—Texture of the Husk—Colour of Barleys—Shape, Size and Structure of the Grain—Regularity in Barley—Damaged Barley—Germination—Barley Drying—Blending of Barley.

FUNGOID DISEASES AND INSECT PESTS

Fungoid Diseases—Insect Pests—Summary.

V. COMPOSITION AND QUALITY OF BARLEY - - 55

COMPOSITION OF BARLEY

Constituents of Barley—Barley Husks—Starch—Cellulose, Hemicelluloses, Pectins, Gums and Lignin—Nitrogen and Protein—The Proteins of Barley—Factors influencing the Nitrogen Content of Barley—The Ash of Barley.

NITROGEN AND QUALITY

Nitrogen Content and Malting Quality—Nitrogen Content and Brewing Quality—Other Barley Constituents and Quality.

REGULARITY IN THE COMPOSITION OF BARLEY

Regularities in the Protein Composition of Barley—Meaning of Regularity—Effect of Variety on the Protein Relationships—Changes in the Proteins during Maturation of Barley—Changes in the Proteins during Storage and Drying of Barley—Regularities in the Carbohydrate Composition of Barley—Implications of Regularity on Barley Quality.

POTENTIAL EXTRACT OF BARLEY

Composition of Barley and Potential Extract—Prediction of Extract—Direct Determination of the Extract of Barley—Valuation of Barley from Potential Extract and Nitrogen Content—Summary and Extension.

AN INTRODUCTION TO THE BIOCHEMISTRY OF MALT AND WORT

VI. COLLOIDS AND HYDROGEN IONS - - - 78

COLLOIDS

Biochemistry—The Colloidal State—Size of Colloid Particles—Definition of Colloids—Colloidal Systems.

CONTENTS

CHAPTER

SECTION

PROPERTIES OF COLLOIDAL SYSTEMS

Properties Dependent on Active Surface—Adsorption—Filtration—Foams—Electrical Phenomena in Colloidal Systems—Lyophobic Colloids—Lyophilic Colloids—Protection—Summary and Extension.

HYDROGEN ION CONCENTRATION

Ionic Dissociation—Hydrogen Ions—Ionisation of Water—Hydrogen Ion Concentration, p_H —Acidity, Alkalinity and the p_H Scale—Buffers—Buffer Titrations—Ampholytes.

DETERMINATION OF HYDROGEN ION CONCENTRATION

Electrometric Methods—Indicators—Colorimetric Determination of p_H —Summary and Applications.

VII. THE CARBOHYDRATES AND PROTEINS OF BARLEY AND MALT - - - - - 104

THE CARBOHYDRATES

The Biochemistry of Malting—Carbohydrates—Starch—Dextrins—Sugars—Constitution of the Sugars—Pentosans and Pentoses.

PROTEINS

The Proteins of Barley and Malt—Hydrolysis of Proteins—Products of Protein Breakdown—Reactions of the Amino-group—Physical Properties of Proteins—Coagulation of Proteins—Determination of the Nitrogen in Wort—Summary.

VIII. ENZYMES - - - - - 119

GENERAL PROPERTIES OF THE ENZYMES

The Nature of Enzymes—Enzymes as Catalysts—Soluble and Insoluble Enzymes—Enzymic Activity—Effect of External Conditions on Enzymic Activity—Activating and Inhibiting Substances—Nomenclature of Enzymes.

THE ENZYMES OF BARLEY AND MALT

Function of the Enzymes—Diastase—Cytase—Maltase—Invertase—Proteolytic Enzymes or Proteases—Isolation of Enzymes by Adsorption—Papain—Phosphatases—Lipase—Catalase.

THEORIES OF THE NATURE OF DIASTASE

α - and β -amylase—Sisto- and Eleuto-amylase—Summary.

CONTENTS

CHAPTER

SECTION

M A L T

IX. FROM BARLEY TO MALT - - - - - 140

CHANGES IN COMPOSITION DURING MALTING

Composition of Malt—Modification.

THE DEVELOPMENT OF ENZYMIC ACTIVITY DURING MALTING

Changes in Diastatic Activity—Proteolytic Enzymes—Development of Cytase during Malting.

CHANGES IN BARLEY COMPOSITION DURING MALTING

Balance between Enzymic Breakdown and Synthesis during Malting.

THE CARBOHYDRATES OF MALT

Starch—Cold Water Extract of Malt—Sugars of Malt—Changes in the Hemicelluloses during Malting.

THE NITROGEN OF MALT

Migration of Nitrogen during Malting—Nitrogen Content of Barley and Malt—The Proteins of Malt—Proteins of Six-rowed Malts—Hordein of Malt—Products of Protein Breakdown—Soluble Nitrogen and Barley Variety—Conditions of Germination and Permanently Soluble Nitrogen—Proteolysis on the Kiln.

MINERAL CONSTITUENTS OF MALT

The Ash of Malt—The Phosphates of Malt—The Acidity of Malt—Formation of Buffers during Malting.

OTHER MALT CONSTITUENTS

Changes in the Fat of Barley during Malting—The Tannin of Malt—Influence of Husks on Wort and Beer—Summary.

X. COMMERCIAL ANALYSIS OF MALT - - - - - 167

Types of Malt—Physical Character of Malts—Objects of Malt Analysis—Standard Methods of Analysis—Sampling—Moisture Content—Extract of Malt—Colour—Cold Water Extract—Forced Malt—Diastatic Activity—Relation between English and Congress Analyses—Summary.

XI. BREWING QUALITY OF MALT AND INTERPRETATION OF MALT ANALYSES - - - - - 180

CONTENTS

CHAPTER

SECTION

MODIFICATION OF MALT

Malt Quality—Physical Tests for Modification—Modification of Malt and its Brewing Value—Colloidal State of Malt Constituents—Analytical Determination of the Degree of Modification—Extract of Coarse and Fine Grist—Cold Water Extract—Products of Protein Breakdown—Coefficient of Modification.

INTERPRETATION OF MALT ANALYSES

Nitrogen Content of Malt—Use of Permanently Soluble Nitrogen Determination—Yeast Nutrition—Application of Extract Prediction Equations—Summary.

XII. TYPICAL MALT ANALYSES AND THEIR INTERPRETATION - - - - - 194

ALE MALTS

Analytical Criteria of the Quality and Brewing Value of Malts—English Pale Ale Malts—Mild Ale Malts—Defective Malts—Other Two-rowed Malts—English Six-rowed Malts—Californian Malts, English made—Other Six-rowed Malts.

LAGER MALT

Manchuria-Oderbrucker Malts—European Lager Malts—Lager Malts, Congress and Institute Analyses.

SELECTION OF MALT ON ANALYSIS

Analytical Criteria—A Suggested Basis of Classification for Malts—Summary.

XIII. SPECIAL MALTS AND UNMALTED CEREALS - - - 208

Use of Special Malts—Colour and Aroma of Malts—Melanoidins.

COLOURED MALTS

Roasted Malts—Black Malt—Brown and Amber Malts—Crystal or Caramel Malts—Analysis of Coloured Malts.

SPECIAL MALTS

Dixon's Enzymic Malt—Diamber Malt—Wheat Malt—MalTED Oats and Rye—Malt Extract.

UNMALTED CEREALS

Malt Adjuncts—Raw and Prepared Grain—Composition of Cereals—Grits—Refined Grits—Flakes—Composition of Grits and Flakes—Use of Grits and Flakes—Summary.

CONTENTS

CHAPTER

SECTION

SUGAR, SPECIFIC GRAVITY, EXTRACT AND POLARIMETRY

XIV. BREWING SUGARS - - - - - 230

Sugar as Malt Adjuncts—Cane Sugar—Invert Sugar—Starch Sugars—Priming and Copper Sugars—Caramel.

SPECIFIC GRAVITY AND EXTRACT

The Metric Unit of Volume—Density and Specific Gravity—Saccharometers—Brewers' Pounds—Extract—Solution Divisors—Balling and Plato Tables—Use of Refractometers.

OPTICAL ACTIVITY AND REDUCING POWER

Polarimetry—Saccharimeters—Optical Activity of Sugars—Reducing Power of Sugars—Analysis of Sugar Mixtures—Summary.

H O P S

XV. CULTIVATION AND TREATMENT OF HOPS - - - 250

HOPS AND THEIR PRODUCTION

Use of Hops—The Hop Plant—The Cone—Hop Growing—Ripeness of Hops—Hop Drying—Packing and Marking—Storage of Hops.

DISEASES AND INSECT PESTS OF THE HOP

Fungoid and Virus Diseases—Downy Mildew (*Pseudoperonospora humuli*)—Hop Mould—Other Fungus Diseases—Virus Diseases—Hop Aphis—Red Spider—Summary.

XVI. USEFUL CONSTITUENTS OF HOPS - - - - 266

THE RESINS

Constituents of Hops—Antiseptic Properties of Hops—Humulon and Lupulon—Properties of the Resins—Biological Methods of Analysis—The Log Phase Method of Analysis—Effect of Hydrogen Ions on the Antiseptic Power of Hops—Fractionation of the Resins—Gravimetric Methods of Analysis—The Preservative Value of Hops—Colorimetric Analysis of Hops—Comparison of Biological and Gravimetric Grading—Validity of Analyses.

OTHER HOP CONSTITUENTS

Hop Oil—Hop Oil in Brewing—Commercial Hop Oils—Hop Extracts—Hop Tannin—Soluble Nitrogen of Hops—Pectins—Summary.

CONTENTS

CHAPTER

SECTION

XVII. TYPES OF HOPS AND THEIR BREWING VALUE - 287

TYPES OF HOPS

Varieties of Hops—English Varieties—Goldings—Golding Varieties—Fuggle's Hop—Breeding New Varieties of Hops—English Hop-growing Districts—German Hops—Czechoslovakian Hops—Yugoslavian and Polish Hops—French and Belgian Hops—American Hops—British Columbian Hops—Australian and New Zealand Hops.

BREWING VALUE OF HOPS

Physical Examination of Hops—Flavouring Properties of Hops—Relative Preservative Power of Different Varieties of Hops—Preservative Value of Different Grades of Hops—Preservative Substances in Wort and Beer—Preservative Value of Dry Hops—Contamination of Hops—Summary, Selection of Hops.

W A T E R

XVIII. BREWING WATERS - - - - - 309

PURITY OF BREWING LIQUORS

Water Supplies—Substances Dissolved in Water—Contamination of Water Supplies—Chemical Analysis—Microscopical Examination of Waters—Bacterial Contamination—Iron Bacteria and Iron in Water—Heavy Water and Rare Elements.

MINERAL CONSTITUENTS OF BREWING LIQUORS

Analysis of Water—The Millival—Expression of Analytical Results—Saline Constituents of Water—Hardness of Water— p_h of Waters.

BREWING LIQUORS

Typical Brewing Liquors—Burton-on-Trent Waters—Type A, Burton-on-Trent Water—Type B, Dortmund Water—Type C, Edinburgh Water—Type D, London M.W.B. Water—Type E, Dublin and Munich Waters—Type F, London Deep Well Water—Type G, Pilsen Water—Types of Brewing Liquors.

XIX. LIQUOR COMPOSITION AND BEER CHARACTER - 333

SALT EFFECTS

Influence of the Liquor on Wort Composition—Reaction of a Malt Mash—Phosphate Reactions in the Mash Tun—Effect of Phosphate Reactions on the p_h of the Mash—Effects of Ions in Brewing Liquor—Buffer Action of Bicarbonates.

CONTENTS

CHAPTER

SECTION

INFLUENCE OF THE LIQUOR ON THE CHARACTER OF BEER

Influence on Flavour—Gypsum Requirements—Magnesium Salts—Buffering of Wort—Influence of the Liquor on Enzyme Action—Salts in Sparge Liquor—Salts of the Alkali Metals—Physiological Effects of the Salts.

CLASSIFICATION OF BREWING LIQUORS

Carbonate Ratio—Less Satisfactory Brewing Liquors — Saline Waters — Nitrate-containing Waters—Sodium Sulphate Waters—Alkaline Waters—Summary.

XX. LIQUOR TREATMENT - - - - - 354

WATER SOFTENING AND DECARBONATION

Water Purification and Treatment—Decarbonation by Boiling—Decarbonation by Addition of Lime—Base Exchange System of Softening—Electro-Osmose—Softening of Boiler Feed Waters.

TREATMENT OF BREWING LIQUORS

Empirical Methods of Treatment—Liquors for Top Fermentation Beers—Empirical Treatment of an Alkaline Liquor—Liquors for Lager Beers—Treatment by Combination of Softening and Acid Addition—Liquor for Lager Beer of Munich Type.

METHODS OF LIQUOR TREATMENT BASED ON p_H CONTROL

Theoretical Basis of Treatment—Neutralisation with Acid—Automatic Plant for Acid Treatment—Lactic Acid Treatment—Liquor Treatment with Lime and Acid—A Test for the Effect of Liquor on Wort p_H —Control of Liquor Treatment—Treatment of Sparge Liquor—Summary.

	PAGE
NAME INDEX - - - - -	495
SUBJECT INDEX - - - - -	497



Photo - K. Hubschmann, London

FIG. 2

THE QUEEN'S COLLEGE BREWERY, OXFORD
MASHING

Facing page 11

CHAPTER I

HISTORICAL

(1) An Ancient Brewery.

There is a record in the archives of the Queen's College, Oxford, of the appointment of a brewer in 1340, the date of the foundation of the College itself, and ever since that time the traditions of mediæval brewing have been kept alive in the little brewery where so much good ale has been produced to the great content of the Fellows and Scholars. The passing of innumerable similar breweries at Colleges, Monasteries, great private houses or inns has left that of the Queen's College almost alone, to brew in the manner practised before the advent of machinery and science transformed a domestic craft into the highly specialised art and business of to-day. The brewery, a beautiful old building some 55 ft. by 22 ft., partly of stone and partly of wood, with a roof of Stonesfield stone tiles, stands at the west end of the Fellows' garden, and, it is to be hoped, will be preserved for its educational value as well as for its unique historical interest as a survival of old English domestic life.

The photographs reproduced show the elements of brewing as they persist to this day. Ten barrels of liquor were, and still are, let down from a wooden back into the copper, raised almost to boiling and then run down a wooden trough into the oak mash tun where formerly they remained until the steam had sufficiently dispersed for the brewer clearly to see the reflection of his face, a temperature now recorded as about 168° Fahr., 28 bushels of malt from sacks delivered after grinding by the local miller were tipped into the tun and mashed with oars and rake. "Many were so sagacious," according to a brewer of 1750, "as to grind their brown Malt a Fortnight before they use it, that it may become mellowed by losing in a great measure the Fury of its harsh fiery Particles, and its Steely Nature, by which a greater Quantity and stronger Drink may be made and be much smoother and better tasted. Best Pale Malts will be fit for Use at a Week's End because the Leisureness of their Drying endows them with a softness and supplies in them what time and Air must do in the brown Sorts."

§ 2 BREWING : SCIENCE AND PRACTICE

The mash tun has no false bottom, but metal strainers cover the two spend pipes through which the wort is run off to an underback after two hours' stand. A hand pump, bearing the date 1778, with a wooden bucket working in a lead barrel, is still employed to raise the worts from the underback through lead pipes to the copper. A second mash is made with cooler liquor (at about 90° Fahr.) and the two lengths are boiled separately with 26 lb. of hops for the whole brew.

From the copper the worts are run down a wooden trough to two shallow wooden coolers holding about six barrels each. The time required for cooling varied from 2 hours to 12 or more according to the weather, and the worts were pitched at high and varying temperatures. This has been regularised at 68° since the introduction of thermometers and facilitated by use of a movable cold liquor coil laid flat in the cooler. The total length of nine barrels is fermented for about 24 hours in the fermenting vessel, from which it is then ladled into casks and rolled into a cellar, where the temperature remains constant at about 55°. The casks are set up on gentries and during the first three days the yeast works from the open bung hole, pouring down their sides into a yeast trough, from which clear beer is ladled back for topping up, the casks being finally filled from one set aside for that purpose. After about six days the beer was transferred, with a few handfuls of dry hops, to upright three-barrel butts to clarify and drawn off after a few days, two or three weeks or a year according to its strength. These curious casks shown in the photograph of the cellar have had to be discarded through age, and the beer is now racked into ordinary small casks with a couple of handfuls of hops.

The beer described is the 25 lb. (1070) College Ale, but a stronger 50 lb. (1139) Chancellor Ale was and is still made in October or March, for which 2½ barrels of the first worts are boiled 3 hours with 20 lb. of hops, which are subsequently re-boiled in College Ale. This beer is stored for a year and drunk on special occasions in the Hall from two-handled silver mugs which, at the undergraduates' tables, are handed round like a loving cup.

(2) Theoretical Speculation.

The Queen's College Brewery represents the position attained, solely by art and tradition, when the great firms of to-day were in their infancy, but the seventeenth and eighteenth centuries were an age of scientific speculation and experiment with novel apparatus. Brewing, which presented so many remarkable phenomena, could not fail to excite the liveliest interest in scientific circles as well as among its practitioners. Theories based on the



FIG. 3
THE QUEEN'S COLLEGE BREWERY, OXFORD
MASH TUN AND MASHING RAKE



FIG. 4
THE QUEEN'S COLLEGE BREWERY, OXFORD
COPPER AND WORT PUMP

(Facing page 2)



Photo: Gillman & Soane, Oxford

FIG. 5

THE QUEEN'S COLLEGE BREWERY, OXFORD
TUNNING

flimsiest evidence, at first very like those of the alchemists and their successors, the physician chemists and phlogistonists, held the field and books were filled with the quaintest notions. Brewing is, indeed, littered with the débris of discarded hypotheses and a warning against reliance on the best authenticated theories is as necessary now as it was at any time. None of them is sacrosanct, and the rapid advance of science has made it only too evident that the accepted notions of to-day are liable to be proved incorrect or incomplete to-morrow. If this is forgotten they may cramp one's style and bind practice with such rigid bonds that little advance is possible, but properly used they give life to the dry bones of scientific fact and are capable of rendering valuable assistance, as well to the practical man as the research worker.

The application of scientific instruments in breweries came comparatively late and it was not until 1760 that brewers began to appreciate the value of the thermometer. James Baverstock, a pioneer of the new instrument, had to conceal and use it by stealth, his father objecting vehemently to such experimental innovations. W. H. Roberts recorded in the *Scottish Ale Brewer* of 1837 that "Baverstock made many valuable discoveries till at length his continued success overcame in great measure the prejudice against the hydrometer and the celebrated Dr. Samuel Johnson was induced occasionally to be present when his experiments were performed." These he had himself described in 1785 after about 17 years' experience with the instrument, but it was John Richardson who invented the saccharometer at about the same date. According to Richardson in 1805, "the darkness in which the business of brewing is involved extends even to the legislature itself, as is evidenced by the frequent disputes between brewers and officers of the Excise, on the subject of distinguishing worts chargeable with the strong beer duty from those which are to be charged only as small, the officer's only means of discriminating consisting in dipping his fingers into the wort, tasting it, etc."

Richardson's method of graduation was very simple and practical. He actually weighed a truly gauged half barrel of water and wort and marked the weights required to sink the saccharometer to the same point according to the difference in weight of a barrel. Thus a weight representing 39 brewers' pounds per barrel would be required when the barrels of water and wort weighed 360 and 399 lb. respectively and "is representative of the difference made to the density of the wort by the accession of fermentable matter." Dring and Fage, Diccass, Bates and Long followed Richardson with instruments on a similar principle, but in Scotland an instrument registering specific

§ 3 BREWING: SCIENCE AND PRACTICE

gravity was made by Allan according to Professor Thompson's design. This was adopted by the Scottish Board of Excise in 1815 and gravities were expressed in degrees in Scotland, instead of in pounds as was customary in England. The introduction of these two instruments produced a veritable revolution in brewing and, for the first time, brought some semblance of exactitude into what had hitherto been based on guesswork.

(3) Fermentation.

No part of brewing has seemed more mysterious than fermentation. "How staggered, even at this enlightened era, would some experienced brewers be, were they asked this one simple and plain question: 'In what does fermentation consist?'" So wrote Dr. Shannon in 1804. The position in 1837 was summed up by W. H. Roberts, who wrote: "Discussion of the subject of fermentation would be of little real benefit to the operator; for confidently as many have asserted their knowledge of its secret causes and effects, the mystery in which its principles are involved continues to present an unpenetrated barrier; those who dogmatically profess to have encompassed this subtle and complicated subject only prove the extent of their ignorance and presumption." This was written just about the time when one of the most acrimonious disputations in scientific history commenced between those who claimed that yeast was a living plant and those who held that fermentation was nothing more than a chemical process.

Combrune defined fermentation in *The Theory and Practice of Brewing*, 1761 and 1804, as "the sensible internal motion of the particles of a mixture, by the continuance of this motion particles are gradually removed from their former situation, and after some visible separation, joined together in a different order and arrangement so as to constitute a new compound." No doubt the germ of a chemical theory, but worked out in a very archaic manner by one whose ideas of the "particles" of a compound were linked to "principles" which could be appreciated by such properties as were typified by spirit, earth, salt, oil, etc. "Vegetable fermentation is that act, by which oils and earth, naturally tenacious, by the interposition of salts and heat, are so much attenuated and divided, as to be made invisible with, and to be suspended in, an homogeneous pellucid fluid." Again Combrune wrote that it was "the acid particles of the air which insinuate themselves into the wort, act on the oils, and excite a motion and effervescence, which is the cause of heat. As the internal motion goes on the particles of the wort become more pungent and spirituous, become more fine and active: some of the more volatile ones fly off, hence that dangerous vapour called gas. The pressure of the



FIG. 6
THE QUEEN'S COLLEGE BREWERY, OXFORD
CLEANSING CELLAR

(Facing page 4

external air, from the very first of its fermenting, not only occasions the particles of wort to arrange themselves in their due order, but also by the weight and action of that element, grinds and reduces them into smaller parts. That this operation persists even after the liquor becomes fine is evident, for every fretting is a continuance of fermentation. It would seem that the more minutely the parts are reduced, the more pungency will appear, and the easier their passage be in the human frame. Lastly, in the final state of all, the active principles being entirely evaporated, a pellicle forms on the surface, seeds deposit from the air, and a moss grows." In all this there is no hint of chemical change, as it is now understood, but merely a refinement of pre-existing principles and their separation from grosser, earthy or oleaginous particles.

(4) The Advance of Chemistry.

Chemistry was, however, making considerable headway at that time (1805). John Richardson said that "fermentation does not set at liberty but positively creates the spirituous parts of the liquor," and Shannon wrote, about the same date, that "saccharine matter was changed into hydrogen, oxygen and carbon, which, after they had been disentangled from their original bonds, united again as alcohol and fixed air." Again, "Fermentation was Nature's way of decomposing and recombining the constituents of fermentable substances in presence of sufficient water; it was allied to respiration and was evidently a low form of combustion." Shannon approached Liebig when he maintained that "yeast was merely exceedingly unstable matter which by its own decomposition would set up the intestine motion in other substances with which it was brought in contact. Vinous fermentation, acetous fermentation and putrefaction were all revelations of the same process. Acetous fermentation destroyed the inflammable spirit produced by the vinous and putrefaction annihilated the whole. The one passed directly into the other in brewing unless the acetous fermentation is arrested by reducing the temperature at tunning."

Shannon also propounded a comprehensive theory of malting and brewing which, in some ways, foreshadowed enzyme action. "Malting was a vegetable degree of fermentation which resolves the glutinous and unfolds the saccharine matter in order to dispose the mucilage to ferment by causing the whole of the farina to dissolve. It is the first stage of decomposition or fermentation, in which the whole principles of the grain are more uniformly mixed to facilitate fermentation, which was only required to blend to advantage the saccharine and mucilaginous parts of the

§ 5 BREWING : SCIENCE AND PRACTICE

grain into one homogeneous fluid called beer and dissipate or throw off the gluten under the form of yeast and lees."

Tizard, a convinced supporter of Liebig, wrote as late as 1875 that "nothing can be more absurd than the idea that the vinous, acetous, and putrefaction fermentation require three distinct ferments." "The power of gluten to attract oxygen is increased by contact with precipitated yeast in a state of decay, the unrestrained access of air is the only other condition necessary for its own conversion into the same state of decay, that is for its oxidation. On this indubitable circumstance, as upon an unshatterable basis, he (Liebig) builds his solution of one of the most beautiful problems of the theory of fermentation."

Fermentation commenced spontaneously in wine because there was sufficient air and heat present to set the particles in motion. The position in respect of wort was different because a great part of the air in barley was expelled in the malt kiln and wort lost this activating agency when boiled. It was consequently necessary to add a ferment "to excite the separation and new arrangement on which the perfection of the product depends and prevent the accidents to be apprehended from worts' disposition to ferment spontaneously through slow absorption of air from the atmosphere." Yeast was the very thing for the purpose, being, according to Combrune (1758), "bladders of the coarser oils of wort, filled with air and ready to start the motion." He therefore recommended that all the yeast should not be added at once so that "the air bladders, all bursting at once, should prevent that gradual action which is the aim of nature." Richardson (1805) held that "the grosser parts of the wort having by this violent commotion been completely separated and the finer recomposed, the more weighty of the former fell to the bottom, whilst the lighter, consisting principally of the refuse mucilage, are carried to the top, where, by their glutinous adherence to each other, being supported by the collected fixed air, they form a yeasty head."

Tizard, following Liebig, stated that yeast was oxidised gluten in a state of putrefaction which induces a similar transportation in the elements of sugar. "The gluten, which is the principal nitrogenous constituent of the native gluten, being activated by an innate and sleepless propensity, is among the first constituents to decompose by absorbing a surcharge of oxygen from the atmosphere, or from the sugar, as the constituency may allow, and to commence decaying."

(5) Ferments.

Two very striking advances marked the first half of the nineteenth century, the discoveries of diastase and of the true nature

of yeast. The former appears to have been absorbed into the literature of brewing before the implications of the latter were realised, not so much, perhaps, on account of its six years priority as because the latter was so directly opposed to earlier theories which prevailed because of the authority of their champions, led by Liebig. In 1830 Dubrunfaut had converted starch to sugar by means of an extract of malt. Three years later, Payen and Persoz precipitated and dried an active substance from similar extracts and called it Diastase. By 1848 the idea of diastase had gained such ground that Tizard made it the main thesis of his *Theory and Practice of Brewing*. He revived the very old idea that beer should be brewed without boiling, as it was "illogical to destroy the inherent fermenting principle and then add yeast." Muspratt held that diastase was generated during germination, and, in the mash tun, converted starch into dextrin and then into glucose. He believed that the gluten of grain had similar, but much less active, converting properties and suggested that diastase was the gluten of the grain in one of its earliest stages of decomposition.

(6) The Nature of Yeast.

From the time when Lavoisier revealed the outlines of the chemistry of fermentation, scientific men were fascinated by the nature of the chemical changes, but as years went by the germ of the biological theory, planted by Leeuwenhoek in 1680, came to fruition. Thénard in 1803 stated that yeast was the cause of fermentation and held it to be of animal origin, but it was not definitely proved that yeast originated fermentation until Cagniard de la Tour, Schwann and Kützing, independently and almost simultaneously between the years 1836 and 1838, solved the problem and declared that yeast was a vegetable organism. Despite the opposition of Berzelius and Wöhler and the widespread acceptance of Liebig's theory (1839) that fermentation was brought about by an unstable body, called the ferment, and was essentially a chemical process produced by communication of instability from one substance undergoing chemical change to another, a sense of doubt must have existed. William Black reflected this in his *Practical Treatise on Brewing* (1849-1866) by saying that Turpin had lately shown fermentation to be an act of vegetation, while quoting in a non-committal manner Liebig's refutation.

Muspratt, another English chemist of the time, said that the fungoid character of yeast was generally admitted and its action in inducing fermentation well understood, though he still apparently remained a follower of Liebig. He, or Böttinger of Allsopp's Brewery, who wrote the article on brewing in his *Chemistry as*

§ 7 BREWING : SCIENCE AND PRACTICE

Applied to Arts and Manufactures, thought that knowledge of the life history of yeast was still incomplete and referred to many attempts made to discover the plant in its perfect condition. "Such was the notion that led Turpin, in the ardour of scientific zeal, to spend a night in a brewery in order to trace out the successive steps in the germination of the yeast plant." Even this self-sacrifice was unavailing as he failed to discover the fungus in its perfect state. Muspratt stated that the plant grows at the expense of the sugar, giving out carbonic acid and leaving alcohol. The living plant was required to sustain the fermentation process.

These quotations are all previous to any hint of Pasteur's discoveries, indeed Muspratt makes no reference to him in his articles on alcohol or beer. It would appear therefore that some brewers in this country were quite prepared for the new biological interpretation of fermentation. It might very possibly not have encountered such opposition from the leading chemists of the day if they had studied the quantitative aspect of yeast reproduction in English breweries instead of Bavarian, where bottom fermentation was then in its early development. Turpin (1840) had evolved a theory that seems to fall midway between that of Liebig and pure vitalism. It was to the effect that microscopically invisible particles of the juice of living plants, still endowed with the power of movement and vitality, were capable of uniting until they ultimately produced the various elementary organs of future living tissues. This was contrary to Liebig's theory that albuminoid substances were themselves the ferments, substituting for it the view that living ferments originated from them in the presence of air.

(7) Pasteur.

A new era opened in 1860 when Pasteur published the results of his enquiry into yeast which was commenced in 1857. He found that sugar was not decomposed exactly according to Gay-Lussac's equation, but that 0.5–0.7% of succinic acid (1857) and from 2.5 to 3.6% of glycerol (1858) were produced at the same time. The fundamental outcome of this investigation was, however, the doctrine that fermentation was coincident with the life of an organism. This was a universal doctrine for all fermentations, whether by yeast, lactic or acetic bacteria and led to demolition of the theory of spontaneous generation (1868). His *Etudes sur le Vin* led to elucidation of the cause of bacterial defects in beer and to proposals for preventing them and, soon after, pasteurisation was applied to beer in Bavaria. The disasters of 1870 induced Pasteur to try to teach his countrymen to produce a beer of national recovery, and his book, *Etudes*

sur la Bière, 1876, in which his views are expounded, has had a far-reaching influence on brewing.

We know from Horace Brown's reminiscences of "Fifty years' experiences of scientific method in brewing practice" how little attention was given to Pasteur's discoveries in this country, but how eagerly they were read in Burton. The *Studies on Wine* "came as a ray of light piercing the darkness and illuminating a new path into the unknown." Brown was soon in a position to recognise the bacteria associated with various defects of beer, but, more than this, he observed that the finer qualities of fully matured beers depended to a large extent on the nature of the yeasts which developed in cask and bottle. By 1877 he proved that these were not connected with the yeast of primary fermentation and must have had an extraneous origin, but it was left to a Dane, Emil Christian Hansen, to prove that brewery yeast was a mixture of several species and that defects were caused by wild yeasts. In 1888 he introduced his pure culture yeast into the Carlsberg brewery and a system of fermentation control that has been of inestimable advantage, particularly to lager brewers, though little use of it has been made in this country.

How these discoveries have revolutionised the design of brewing plant, changed the outlook of brewers and given them new ideas on the control of brewing processes, will be told and illustrated in the sequel. Like every other revolution they have roused enthusiasms which have led to excess in some directions and wiped out institutions that appeared to be sanctified only by antiquity but have since been found to be based on solid foundations. Some of these are coming slowly back and the outlook which tended to be restricted to the avoidance of infection is widening to realisation that chemistry and physics must not be overlooked in brewing

(8) The Modern Era.

Even after Pasteur had proved that fermentation was due to the life of an organism, there remained in many minds a deeper problem. How did yeasts perform their task and what were the agencies behind its manifestations and those of every other living thing? Liebig had capitulated to the extent that in 1870 he wrote that the importance of the living organism in fermentation was clearly due to the fact that it was only through its intermediary that the albuminate could be brought into transitory but intimate association with the sugar necessary to pass on the motion by which the sugar was decomposed. Pasteur accepted the view that his work was not finished by the mere statement that fermentation was the result of life without air. He and many more sought for the

meaning of this life and the mechanism through which it worked, but it was not until 1897 that Buchner found the connecting link between Liebig and Pasteur in the discovery that fermentation was possible without the intervention of living cells. He extracted from yeast the enzymes on which its life depended and gave impetus to a vast amount of scientific investigation which has been of inestimable value in medicine, nutrition and many other branches of modern science.

Concurrently with the stormy disputations on the cause of fermentation have been a whole series of discoveries in the chemistry of brewing materials and their transformations. Discoveries which have played a large part in establishing the branch of chemistry now known as biochemistry. The advance in this branch of knowledge has been enormous in recent years, and much of it has its applications in brewing, as will be detailed in later chapters. It is not only that brewing has shared in the fruits of advancing knowledge, but interest in its many phases has provided the momentum to extend science in ways that have proved of benefit to mankind.

(9) Barley as the Raw Material of Brewing.

Barley was no doubt employed in the preparation of fermented liquors long before the dawn of recorded history, when it was the chief cereal used for food. Beer is known to have been widely drunk in Ancient Egypt and has been traced back to the age of the pyramids, some four or five millennia B.C., but recent investigations suggest that the Egyptians learnt the art of making it from the peoples of the valleys of the Tigris and Euphrates, where beer played a large part in domestic economy 5,000 or 7,000 years B.C. Barley was the predominant cereal of the ancient world, the basis of barter and exchange in Chaldea 3,000 to 5,000 years B.C., and, when displaced by spelt for bread making, it still retained its pre-eminence as the raw material of brewing and has continued to do so except in countries where the abundance of rice placed that cereal in an unassailable position as the source of the national fermented beverage. The use of barley for brewing is, however, not based on traditional usage alone. It has technical advantages which place it before all other cereals for that purpose. It differs from all the other common cereals in that the husk adheres to the corn after threshing, as it did in spelt, wheat being a much later labour-saving introduction. This renders malting and subsequent extraction of the fermentable wort much easier of accomplishment than with wheat or other grain. It grows well in countries in which the vine, rice or palm cannot be cultivated and being a storehouse of starch,

which can be converted readily and naturally to fermentable sugars, together with proteins, ash and other valuable constituents, it has proved the logical source of the national beverage of those countries.

Barley was not always malted, but some form of incipient germination had to be resorted to in order to liberate the enzymes required to convert the starch to soluble, fermentable products. This is still carried out by the Fellah of Egypt in a manner which must resemble that employed by his ancestors. Barley is moistened in a suitable earthenware container or buried in the soil until germination starts, when it is crushed with a pestle or roughly ground and made into large loaves with some sour dough or leaven. These are baked but only until the surface is formed into a crust, leaving the interior in an unbaked condition. When beer is required the loaves are broken up, mixed with water in a pot and allowed to ferment. The liquid is pressed and sieved from the dough and when fermentation is completed produces the acid beer known as Boozah. A more advanced stage in brewing, with the beginnings of malting, is also practised. The grain is steeped and allowed to germinate for three or four days in earthenware pans, after which the matted green "malt" is dried on mats in the sun, separated from the rootlets by hand and ground between stones. Ungerminated grain is ground and made into a dough, which in a few hours begins to saccharify and ferment. This is then baked as before and afterwards mashed with water to which a little salt and a proportion of the malted grain is added. Fermentation soon starts and, after sieving, is completed in a few hours, after which lactic acid is formed, coagulates proteins, etc., and leaves a clear liquid in which acetic acid and ethyl acetate are produced from the alcohol, and which will keep unchanged for some weeks.

BARLEY

CHAPTER II

THE STRUCTURE AND CLASSIFICATION OF BARLEY

STRUCTURAL CHARACTERS OF BARLEY

(10) The Ear of Barley.

The differences in the barleys grown in various countries and the gap that separates them from wild barleys indicate the evolution through which they have passed as the result of cultivation in widely separated areas—an evolution equally remarkable as that through which malting and brewing have passed. Variations in the structure of the grain and in its development in different climates are accompanied by differences in composition which, with the resources of the world available, have placed brewers in a position to pick and choose those barleys most suitable for their use. In most countries the local barley must, if possible, supply the main bulk of raw material for brewing, but, where this barley is liable to damage through inclement weather, it is essential that brewers should study the characteristics of the grain of other countries and be in a position to make the best use of a proportion with that of their own, whenever occasion should arise. This applies particularly to England, where a wider range of imported barley is used than elsewhere, and is very helpful in assuring the stability and lasting brilliance of light gravity beers.

Two names will always be closely associated with barley in England. Those of Horace T. Brown and E. S. Beaven. Agriculture, Malting and Brewing are equally indebted to the latter for his pioneering work on the pure line barleys and for Plumage-Archer. The former was a pioneer in the study of the composition of barley and its relation to the quality of beer. This book owes much to both of them, and in this chapter the author has made use of an extremely lucid but rather inaccessible paper on the structure of barley by Horace Brown¹ and followed the classification drawn up by Beaven.

If an ear of barley is examined it will be observed that the corns are attached to a laterally compressed axis or *rachis*, which is jointed at *nodes* forming projections alternately on either side of its length. Each of these projections formed the basis of attachment of three florets, situated side by side across the

flattened side of the axis. Thus, at two adjacent nodes there were originally three florets in a group on one side of the rachis and three on the other, slightly above or below the former group. In one group of barleys all these florets are fertile and produce three corns at each projection, alternately on either side of the rachis, giving a six-rowed barley, as in Fig. 7. In another great group, only the middle floret at each node is fertile and the barley produced is two-rowed, Fig. 8. The remnants of the sterile florets on one side of the rachis can be seen in this photograph and there are two similar rows on the other side.

(11) Wide-eared and Narrow-eared Barleys.

Each of these figures shows two types of barley. In one, the joints on the rachis are closer together than in the other, or, to put it in other words, the internodes are shorter in the former. As a result, the corns are more closely packed on this ear, which is consequently referred to as *dense*, while the other is *lax*. The corns of the dense ear are forced to lie at a greater angle from the axis than in the lax ear, giving *wide-eared* and *narrow-eared* barleys respectively. Thus, four characteristically shaped ears are obtained; wide- and narrow-eared six-rowed barleys, and wide- and narrow-eared two-rowed barleys. The narrow-eared barleys have a greater tendency to nod or bend over when ripe than the wide-eared, on which account they are distinguished as *nutans* and *erectum* in some classifications. If the photograph of the narrow-eared six-rowed barley is examined, it will be observed that the two lateral corns behind the ear are visible between the alternate groups on the front and, if an ear is examined lengthways, it will appear to have only four rows, because the two lateral rows of corns on one side of the rachis partially or entirely overlap the alternate lateral corns on the other side. Six rows of corns actually exist, but the ear has the appearance of four rows. The term four-rowed is consequently sometimes used to describe such barleys although, strictly speaking, no four-rowed barley exists, except a wild form with infertile median rows.

(12) The Barley Corn.

The corns are spindle-shaped and in transverse section give the impression of two lobes formed by the deep indentation or ventral furrow. This shape appears to be due to the tension to which the skins and husk have been subjected during growth of the grain and development of the embryo. If the husk is removed from the back of the corn, the wax-like *embryo* or germ can be seen through the inner transparent skin. It is possible to make

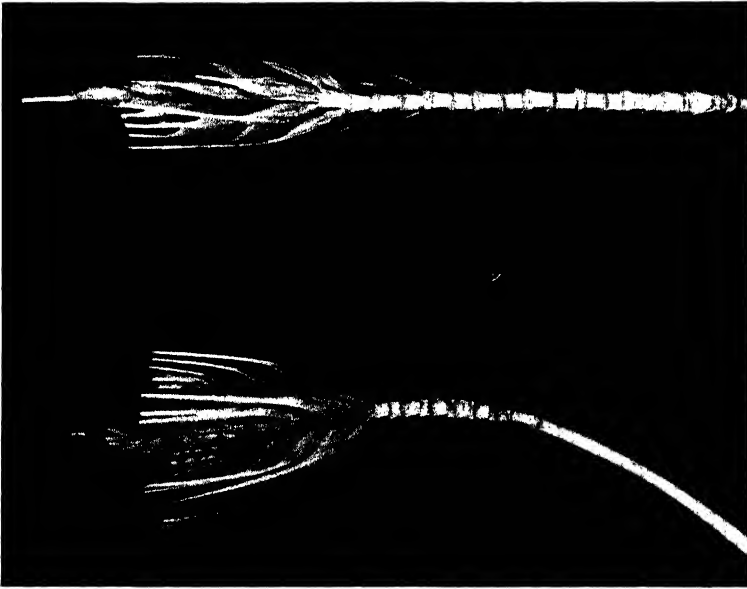


FIG. 7

PARTIALLY STRIPPED EARS OF SIX-ROWED BARLEYS



FIG. 8

PARTIALLY STRIPPED EARS OF TWO-ROWED BARLEYS



FIG. 9
Kernels of VAUGHN, SHOWING RACHILLA



FIG. 10
HOODED BARLEYS. A. NEPAL. B. HORSFORD
(NEPAL \times MANCHURIA)

out the rudiments of the stem and roots if this bud-like structure is dissected with a pocket knife. This living part of the corn occupies about one-thirtieth of the whole grain, the remainder of which consists of the *endosperm*, which is a storehouse of reserve material supplying the germ, which lives saprophytically on it. If the embryo is completely removed it may be made to grow on solid nutrient media, such as gelatin and sugar, provided the scutellum remains undamaged.

(13) Identification of Threshed Barleys.

Close inspection of corns from different kinds of barley will reveal certain differences in structure which are useful for distinguishing threshed barleys of different varieties. Thus, lying within the ventral furrow and attached to the base of the corn is the basal bristle or *rachilla*, shown very clearly in the photograph of Vaughn, Fig. 9. It is actually a continuation of the short lateral stem on which the floret is borne and can usually be made to stand out from the furrow by a gentle pressure of the thumb nail on the base of the corn. It will be found to vary in structure in different barleys. Sometimes it is long with very short hairs. In others it is short with woolly hairs, while in others it is bristly. Two types of basal bristle are shown on the corns of Vaughn reproduced in Fig. 9 from the paper by G. Wiebe, referred to in Section 33. One is of the long-haired type, while the other is very much reduced. About one-third of the corns of Vaughn show this character, so that the basal bristle cannot always be accepted as a definite varietal characteristic, though in many cases most useful. It is so difficult to distinguish closely allied barleys, that note has to be taken of any small variants that may occur.

The structure of the husks and their appendages provide useful characters for distinguishing varieties. The husk enveloping the back of the corn, known as the valve, *palea inferior* or *lemma*, is usually terminated by an awn or beard. In a few varieties the latter is replaced by a hood-shaped structure, as shown in Fig. 10, reproduced from *Bulletin* 1334 of the U.S. Dept. of Agriculture. In some cases the awn is rough or serrated. In others it is smooth. Five nerves, marking the course of vascular bundles, can usually be seen on the lemma, but some barleys, like Trebi, have only a single nerve, while others have two, as in Club Mariout. In some varieties these nerves are serrated, as can be seen in the lateral nerves of Vaughn, Fig. 9, while those of others, such as Hero, are smooth. In most ripe barleys the husk is firmly attached to the outer skin of the seed, but in some cases it is detached as chaff when the barley is threshed, just as it is from wheat and most other cereals. These varieties are known

as *naked barleys* and are difficult to distinguish from wheat when threshed. They are of little or no use in brewing, but justify cultivation in districts where barley is cut green and used as fodder, or they may be useful for pearl barley.

The colour of the mature corns varies considerably from white and yellow to tints of blue, purple, brown and black. In some cases the colour is in the husk, but in others it is due to pigment in the layer of cells or aleurone layer just below the inner skins. The blue in the aleurone layer of some Californian and other barleys gives a greenish tinge to the grain when seen through the yellowish husk. Colour sometimes forms a useful distinguishing mark, but as it is liable to great variation according to the soil and other conditions of growth it is not a reliable varietal character.

Another feature of interest in differentiating barleys, particularly wide- from narrow-eared varieties, is the shape of the point at which the corn articulates with the rachis. As a result of the shortness of the internodes on the rachis of wide-eared barleys, the corns are bent back at a wide angle and in many cases a distinct nick or crease is produced across the dorsal palea of the husk. This is distinctly shown in Wiebe's photograph of Atlas and Mariout barleys in Fig. 11. Since the corns of narrow-eared barleys lie more closely to the rachis, they usually have a narrow point of articulation with a sloping bevel at the base of the dorsal palea. This can be seen in the photograph of Coast barley in the same figure. This feature, though frequently useful for identification of wide- and narrow-eared barleys, cannot always be made out and in the case of Atlas it is not sufficiently definite for identification.

Threshed grain of the six- and two-rowed barleys can be readily distinguished by the shape of the corns. Those of two-rowed barleys are more or less even in size and uniform in shape, while the points of attachment of the three corns at one node of a six-rowed barley are so close together that the lateral corns are twisted to lie snugly against the axis and are rather smaller than the median corns. The proportion of the two kinds in a mixture can be determined by comparing the number of straight and twisted corns. There are two of the latter to one straight corn in six-rowed barleys, as shown in Fig. 11. Six-rowed barleys are also generally distinguishable from two-rowed by their greater quantity of husk.

Despite such distinctive differences as have been pointed out it is frequently impossible to identify the species of threshed barleys or to spot mixtures of closely related varieties. So many hybrids and selections have been produced, which differ only in some physiological or agricultural character, that the classifications based on morphology are becoming more and more useless as a

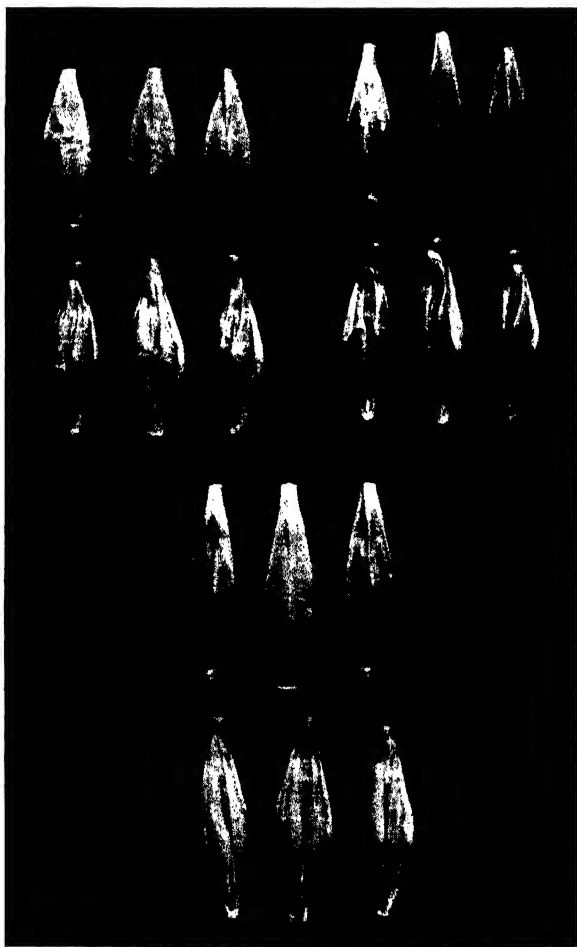


Fig. 11

KERNELS OF SIX-ROWED CALIFORNIAN BARLEYS
ATLAS, COAST, CLUB, MARIOUT

(Facing page 18)

means of distinguishing allied races. As a result, it is, in many cases, necessary to be content with distinctions of *type*, which may or may not differentiate varieties or races. This is not entirely satisfactory, as some of the allied races, which would necessarily be included in one type and bulked for malting purposes, may behave differently on germination and give rise to unevenly grown malt. It is indeed very desirable to acquire the experience by which alone many races can be distinguished and thereby avoid difficulties which may arise from bulking different barleys, which may, unless very carefully scrutinised, be taken to be of the same race, and, what is of even more importance, of equal maturity. Malting and brewing requirements are a matter of physiology, rather than of morphology, so that a classification based on the former would be in every way preferable, were it possible to devise a practical scheme.

(14) Development of the Barley Corn.

It is very instructive to examine an ear of barley at the time it is about to emerge from the sheaf which enfolds it and observe how the ear develops from the florets into a six- or two-rowed form. The florets are arranged in threes alternately on either side of the flowering stem, as already described, and these will be found to be all alike, in which case they are all fertile and produce a six-rowed barley, or the middle floret can be seen to differ from those on either side of it if the barley is two-rowed.

Each individual floret of six-rowed barleys and the median fertile florets of two-rowed are partially enclosed in two long, narrow sheaths, known as empty glumes or outer glumes, which do not become larger as the floret develops. Each of these glumes is prolonged at its tip into a small awn. Within them are two broad membranous sheaths or flowering glumes completely enclosing the vital parts of the flower. Of these, the valve, *lemma* or *palea inferior* is larger than the valvule, *palea* or *palea superior*, which is on the side of the flower nearer to the axis. The latter arises from the secondary axis of the spikelet, comes only partly round the flower and has no awn. The *lemma* springs from the main axis of the spikelet, wraps over the *palea* and round the flower. It provides more morphologically important characteristics than any other single structure in barley and is much used in classifications. It is typically drawn out into a long awn, but some varieties are awnless or hooded. Within the *lemma* are two scale-like structures fringed with long hairs and known as the *lodicules*. These appear to represent the perianth of an ordinary flower. In the centre of each fertile floret is the female organ or ovary, which eventually develops into the corn. It is crowned

by two feathery *stigmas* to collect the pollen deposited from the two-lobed anthers of the three *stamens* or male organs of the same floret. These are carried on slender stalks.

All these structures are well developed by the time the ear, without the awns, is about an inch long, but the florets towards its tip do not develop, so that the mature ear of barley has a truncated appearance. The lateral spikelets of two-rowed barleys resemble these outwardly, but contain no ovary at all, and the three stamens remain very small. They also do not produce awns. The florets are so closely invested by the glumes that self-fertilisation is the rule, though a few florets open for a short time in the morning and permit the anthers to protrude and scatter their pollen, thus suggesting the possibility of cross-fertilisation should it gain access to flowers on other plants, but this seems very rarely to occur, if at all. It appears that the glumes are forced open by the lodicules becoming turgid, but in upright two- and six-rowed barleys flowering nearly always occurs with closed glumes. Open flowering is more common with the nodding barleys and generally also occurs after the ears have grown out of the ensheathing leaf. Flowering does not occur at the same time throughout the ear, but appears to commence at about the centre, spreading upwards and downwards to be completed in three or four days. The anthers split and scatter their pollen over the stigmas nearly always before the glumes separate, after which any remaining pollen is scattered by the wind when the anthers emerge. It is interesting to note that open flowering forms are most liable to infection by fungus spores such as ergot and smut. (W. E. Brenchley.²)

Fertilisation occurs through development of a fine tube on a pollen grain which has become attached to the hairy stigma. This finds its way down the *style* and enters the inverted ovary through an opening, the *micropyle*, at its apex. Here it enters the *ovule*, pierces the *embryo-sac* and mingles its contents with those of the *oosphere* or ovum, which eventually gives rise to the young plant. The ovule has double walls and contains a mass of thin-walled tissue called the *nucellus*, of which one cell, much larger than the others and containing at least eight nuclei, is the *embryo-sac*. Both embryo and endosperm originate in this cell. The fertilised ovum gives rise to the embryo, while the central nuclei of the embryo-sac produce the endosperm. The embryo-sac rapidly increases in size and the greater part of the nucellus and ovary walls is used up as food material for the developing plant, but the outer wall of the nucellus persists, becomes thickened, and probably takes part in the formation of the semi-permeable membrane (Section 15). As the embryo develops the remainder of the embryo-sac becomes filled with thin-walled cells containing



FIG. 12

DORSAL VIEW OF HERO AND VAUGHN BARLEYS,
SHOWING OUTER GLUMES

Facing page 21]

protoplasm, in which starch grains slowly form. These cells are bounded by a triple layer of rectangular cells which contain no starch, but become granulated through production of *aleurone grains* and fatty matter. This constitutes the aleurone layer of the fully developed corn. The ovary grows very rapidly and after about a week ceases to become longer but gets broader and thicker almost until maturity.

The grain of barley thus includes the united product of both ovary and ovule, representing both the seed and the fruit of other classes of plants. The fruit, which is produced by development of the ovary, is reduced to a very thin integument which covers the seed proper, produced from the ovule. Such a combination of seed and fruit is known as a *caryopsis*. At first the young barley corn is quite separate from the flowering glumes, but after about ten days a sticky substance is secreted, except in naked barleys, and fastens the glumes to the young fruit, so that the mature grain consists of the combined kernel and glumes. Water, nitrogen and mineral matter pass into the developing grain almost from the time of flowering, and carbohydrates, mainly starch, are laid down. The nitrogen and ash content reach their maximum two or three weeks before ripening. The green cells of the grain lose their colour and turn brown, the awns remaining green for a longer time. At the same time desiccation occurs, maturation sets in and the barley ripens off. The awns are largely transpiring organs, through which water from the grain is given off. The transpiration current thus produced implies movement of material from other parts of the plant to the ear. This appears to apply particularly to starch, which is reduced in quantity if the awns are cut, as it is also in hooded and awnless varieties. Quite a large proportion of the ash, some 30% of the total, is transferred to the awns, increasing their brittleness, while that of the rachis is reduced.

Since the husks are the remnants of the protecting envelope of the flower, they do not actually belong to the grain and are part of the leaf system of the plant. In addition to these two sheathing leaves or glumes, which are protected by a heavy cuticle, two outer glumes exist at the base of the corn as shown in Fig. 12. These are readily detached and only occasionally seen in threshed barley, but they serve, among other structures, as varietal characteristics. The photographs are of Hero and Vaughn barleys, with smooth and hairy outer glumes respectively.

(15) Microscopic Structure of the Barley Corn.

Many of the details of structure of the barley corn can be made out from the photomicrographs of transverse and longitudinal

sections in Figs. 13 and 14, although it is extraordinarily difficult to obtain a satisfactory longitudinal section without tearing some parts of its delicate structures. The corn is enclosed in the husk, of which the lemma (L) wraps over the edges of the palea (P). Five vascular bundles are cut across in the former and two in the latter. The two lobes and the 'ventral furrow' are clearly seen in the transverse section. In the deepest portions of this furrow (VF) lie some empty cells, which are the only remnant of the nucleus. Here also is the dark coloured pigment string which represents the line of attachment of the ovule to the walls of the ovary. Originating in the pigment string and completely enclosing the grain are three delicate membranes. The outermost, or pericarp (Pe), is the remains of the ovary and corresponds to the covering of a fruit in other plants. The second or testa (T) is the true seed coat and a remnant of the two inner integuments that once existed inside the ovary wall. Finally there is the investing wall of the nucellus, which A. J. Brown³ showed was of importance in malting, since it forms a semi-permeable membrane around the seed through which water can readily pass, though acids, alkalis, salts and most other dissolved substances cannot, iodine being a striking exception. Evidence of this semi-permeable layer can be obtained by immersing corns of blue Californian barley in dilute sulphuric acid. Water is absorbed, but the colour, due to blue pigment in the aleurone cells, is unchanged. If, however, some of the corns are cut or damaged in such a way as to puncture this membrane the sulphuric acid can enter them and will turn the blue colouring matter of the aleurone layer red.

The external layer of the seed proper, known as the aleurone layer (Al), can be seen in both the transverse and longitudinal sections. It is of considerable importance in barley and normally consists of two or three layers of thick-walled, cubicle cells containing the aleurone grains of protein matter, soluble in 10% salt solutions, embedded in protoplasmic material and also minute globules of fat, but no starch. The aleurone layer appears to have a double function, that of a protective layer and a source of nitrogen for the young plant after it is sufficiently developed to derive its carbohydrates from the air by photosynthesis, but before it is able to make use of the nitrogen of the soil by means of its rootlets. It is not attacked during malting and remains unaltered in mash tun grains.

The space within the aleurone layer is mainly occupied by typical storage tissue, consisting of thin-walled cells containing starch granules embedded in a fine network of protein material, the remnant of the protoplasm. This constitutes the major

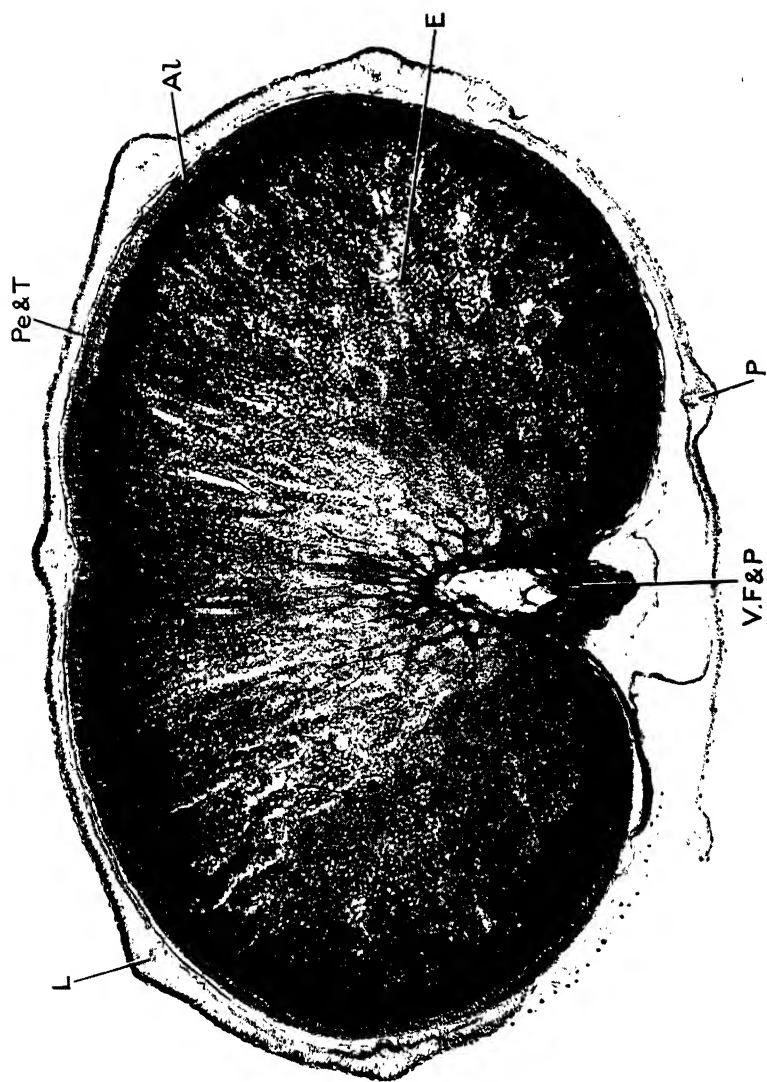


FIG. 13
TRANSVERSE SECTION OF BARLEY CORN ($\times 40$)

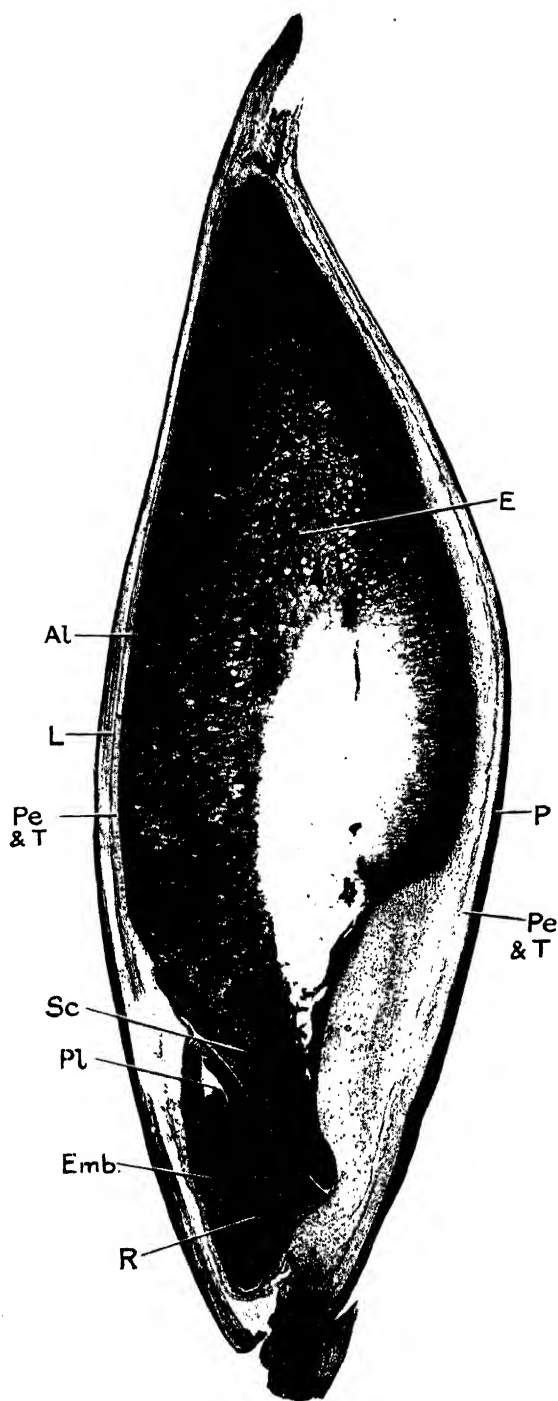


FIG. 14
LONGITUDINAL SECTION OF BARLEY CORN ($\times 17$)

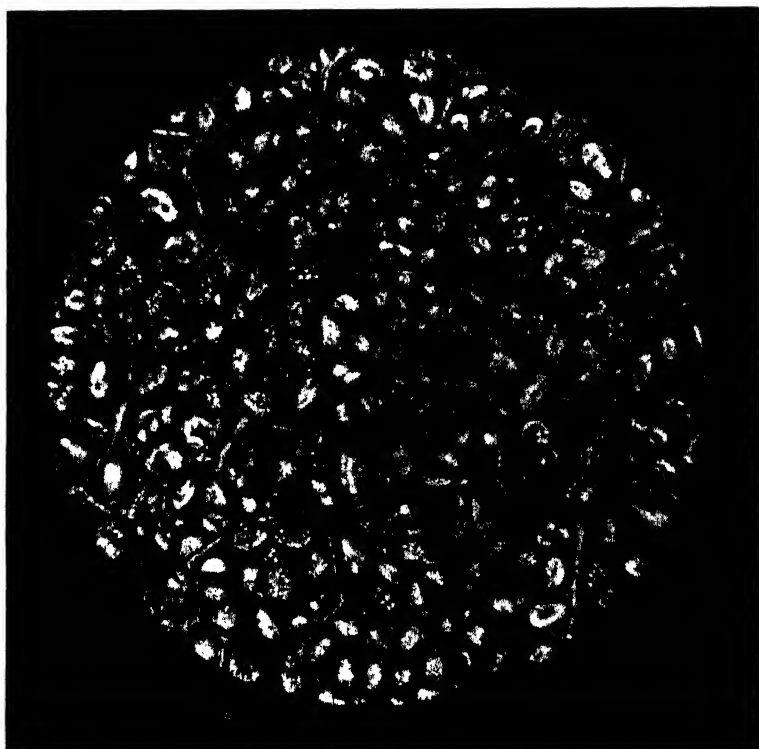


Photo : G. T. Cook

FIG. 15

ENDOSPERM OF BARLEY. TRANSVERSE SECTION ($\times 400$)



FIG. 16
EMBRYO OF BARLEY. LONGITUDINAL SECTION (40)

Facing page 23

part of the endosperm (E) and its structure can be made out from the photomicrograph, Fig. 15.

At the proximal end of the endosperm and partly embedded in it lies the embryo, Fig. 16, containing all the growing elements of the plant to be, as a number of modified organs. The structures which will develop into the rootlets (R) and acrospire (Pl) are clearly visible in the photomicrograph, the former tipped with a root cap and sheathed in a matrix of cells. The latter is known as the plumule.

The embryonic rootlets and acrospire are attached to a mass of tissue which covers the whole embryo like a shield on the side adjoining the endosperm and is known as the *scutellum* (Sc). Its structure is clearly shown in the photomicrograph of part of a longitudinal section of a barley corn, Fig. 17. It represents the *cotyledon* of other plants and consists mainly of thin-walled cells with large nuclei. The surface of contact with the endosperm consists of an *epithelial layer* of elongated cells placed endwise between the endosperm and the main mass of the scutellum, which is held to constitute an absorbing organ, functioning by means of enzymes secreted from its epithelial layer, whereby the living embryo is enabled to derive its nutriment from the endosperm. If the longitudinal section of the embryo is examined it will be seen that the aleurone layer extends only over the endosperm and terminates against the scutellum.

Germination and Secretion of Enzymes. Germination is a continuation of the growth of the embryo which was arrested at the time of ripening of the seed. This growth is at the expense of the carbohydrate and protein reserve materials contained in the cells of the endosperm. Several layers of empty compressed cells next to the epithelial layer are to be seen in the photomicrograph. These, according to Brenchley,⁴ were probably endosperm cells which have been depleted of their contents and crushed back by the growing embryo, but in which starch granules had never been formed.

The epithelial layer is the seat of secretion of the enzymes, which passing out from it permeate the endosperm during malting. Brown and Escombe⁵ held that the cytase which acts on the cell walls during germination originated in the aleurone cells, but this is contested by later investigators (A. Mann and H. V. Harlan),⁶ who maintain that this enzyme, like all others, is secreted from the scutellum and proceeds outwards through the corn. The appearance of greater action in contact with the aleurone layer being due to the enzyme finding there the course of least resistance. The most important factor in enzyme production is, according to Mann and Harlan, the surface area of the secreting organ,

but they also found a difference in the type of cells of the epithelium. In good malting barleys these were long and narrow, with a greater number in a given area. In an inferior malting barley they were short and broad. This was associated with the activity of secretion. Cytase gradually attacks the cell walls of the endosperm, but never entirely destroys them. The cell walls swell up slightly and their stratification becomes much more apparent under microscopical examination owing to partial separation of their three constituent lamellæ. These are gradually disintegrated, but the middle lamella appears to offer a somewhat greater resistance than the others. The cell walls still persist in the most friable malt, but they are difficult to see unless the microscopical preparations are stained with Congo red or some other dye. This action on the cell walls makes them permeable to diastase, which then corrodes the starch granules, while other enzymes attack the protein contents of the cells in which the starch is embedded. Satisfactory malting depends on adequate transformation of the cell walls right to the tip and back of the corn, accompanied by the least possible conversion of the starch granules.

CLASSIFICATION OF BARLEYS

(16) Species and Races.

Barleys are included in the genus *Hordeum* of the natural order *Gramineæ* or grasses. Linnæus recognised six species, thus differentiating wide- and narrow-eared six-rowed barleys, wide- and narrow-eared two-rowed and two species of naked barley. Many later botanists have ranked all these as sub-species or races of one species, for which the name *Hordeum sativum* has been adopted. Others divide barley into four distinct species. The term "variety" is used to distinguish plants belonging to the same species but differing in some structural respect which persists through succeeding generations. Varieties thus have a more or less recent common ancestry and will, by natural or artificial cross-fertilisation with others of the same species, give rise to new varieties generally of intermediate character but occasionally differing widely from either parent. Heaven holds that all varieties of cultivated barley fulfil the latter condition and forms exist intermediate between all the Linnæan species. Variety is used commercially in a looser sense than this to distinguish seed that has been selected through a series of generations by growers to establish uniformity in time of ripening, length of straw or other useful commercial characters which are insufficient to distinguish varieties in the botanical sense and depend largely

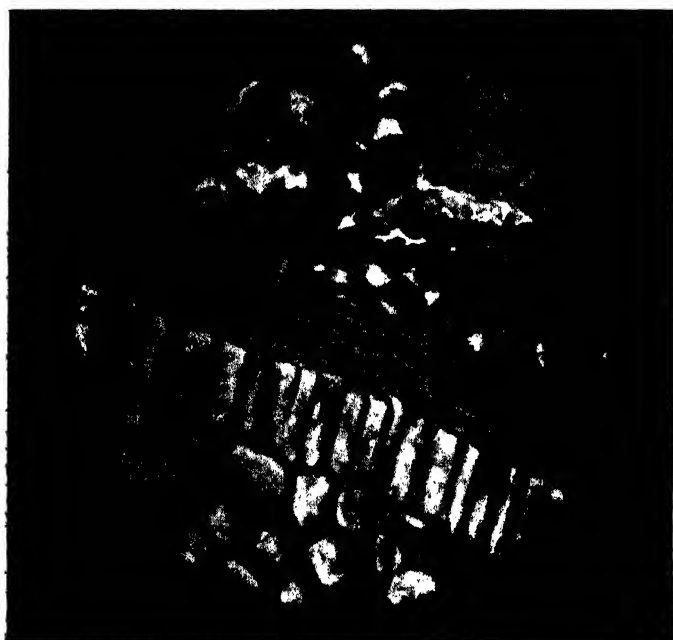


Photo. G. T. Cook

FIG. 17

PART OF THE SCUTELLUM WITH EPITHELIAL LAYER ($\times 400$)

[Facing page 24]

on conditions of soil and climate. It is preferable to describe these as "races."

(17) Classifications.

The classification adopted by Beaven⁷ includes all cultivated barleys in the genus *Hordeum sativum* and divides them primarily into the following sub-species in which fertility and density are used as the main distinguishing characters.

Beaven's Classification of Barleys

Hordeum sativum

(1) Spike of six rows of spikelets, all fertile. Six-rowed barleys.

- | | |
|----------------------------|---------------|
| (A) <i>H. hexastichum.</i> | Wide-eared. |
| (B) <i>H. vulgare.</i> | Narrow-eared. |

(2) Spike of six rows of spikelets, all fertile—two median rows normal, four lateral rows diminutive and without awns. (No malting value.)

H. intermedium. (A) Wide-eared and (B) Narrow-eared varieties which Körnicke considered as two sub-species.

(3) Spike with two median rows of fertile spikelets and four lateral rows infertile or staminate.

- | | |
|--------------------------|---------------|
| (A) <i>H. zeocriton.</i> | Wide-eared. |
| (B) <i>H. distichum.</i> | Narrow-eared. |

(4) Spike with two median rows of spikelets fertile, and four lateral rows rudimentary and without floral organs.

H. decipiens. (Not malting barleys.)

Each of the sub-species includes barleys which differ in the character of the spikelets and their appendages. These are distinguished as varieties. Many of the morphological characters used for this purpose have already been described. The most striking difference is, perhaps, that marked by adherence or non-adherence of the husk, giving the ordinary form with adherent paleæ and the naked barleys. If it were necessary to take cognisance of every possible combination of variations in structure of the lemma and its appendages, in the form of the outer glumes and rachilla, shape of the ear, colour of the grain, etc., the number of varieties would be enormous. Fortunately this is not necessary, but in 1902 Beaven listed 40 natural varieties and 75 hybrid races. The number of the latter might be increased almost indefinitely but comparatively few would be sufficiently distinct or useful to warrant distribution. It is in every way advantageous

to keep the number of races in cultivation as low as possible, compatible with good yield and quality in different localities. Reference must be made to Beaven's original paper for details of the varieties.

A few of the more common and readily recognised forms are illustrated in Figs. 18 and 19. The six-rowed barleys in Fig. 18 are, named according to Beaven's classification :—

F 112	<i>H. hexastichum</i> var. <i>pyramidatum</i>	A winter hardy selection raised by Beaven.
Chilean	<i>H. hexastichum</i> var. <i>parallellum</i>	A barley of the normal wide-eared variety.
July	<i>H. vulgare</i> var. <i>pallidum</i>	A normal narrow-eared, early-ripening selection of Manchuria type.

The three two-rowed barleys of varying density represented in Fig. 19 are :—

Fan or Peacock	<i>H. zeocriton</i> var. <i>zeocritum</i>	A barley which has gone out of cultivation in England.
Goldthorpe	<i>H. zeocriton</i> var. <i>erectum</i>	Moderately dense eared.
Chevallier	<i>H. distichum</i> var. <i>nutans</i>	Typical narrow-eared.

Examples of each of the four principal groups or sub-species of Beaven's classification are represented among British barleys. The wide-eared six-rowed *H. hexastichum* is grown as a winter sort for feed as is the narrow-eared *H. vulgare*, which is also grown as a spring barley. *H. zeocriton* includes natural and hybrid barleys of which Goldthorpe and Plumage-Archer are representative, while Chevallier and Spratt-Archer are typical narrow-eared, two-rowed *H. distichum*. Most of the Continental two-rowed barleys are of the narrow-eared type.

The majority of the six-rowed American and Mediterranean barleys would be included among the narrow-eared varieties of Beaven's classification, but *H. hexastichum* is found in the French *Escourgeon* and mixed with *H. vulgare* in Chilean brewing. Beaven listed the following barleys in the various varieties :—

H. vulgare, vars. *pallidum* and *cærulescens*. Brewing Californian, Brewing Chilean, Mexican, Spanish, Algerian, Tunisian, Morocco.

var. *pallidum*. Yerli Smyrna (frequently mixed with *H. distichum*).

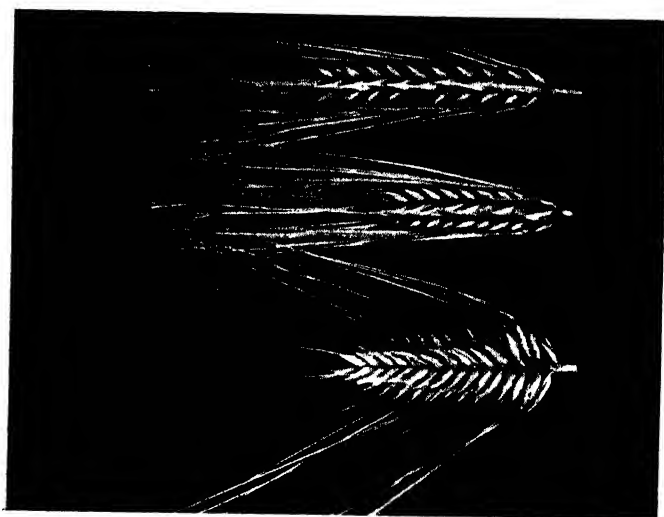


FIG. 18
SIX-ROWED BARLEYS (P 112, CHILEAN, JULY)

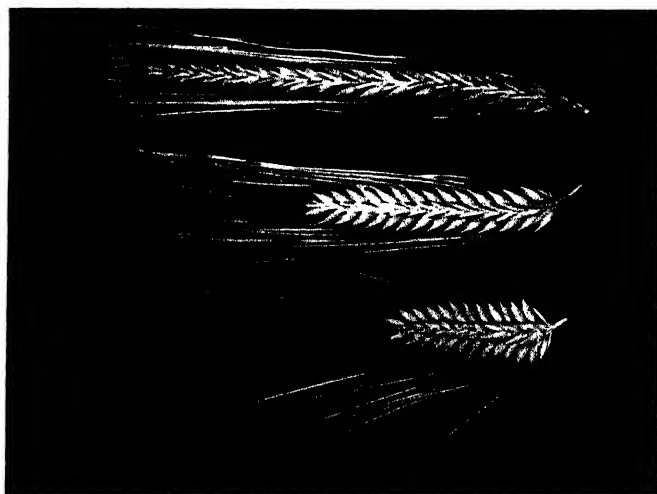


FIG. 19
TWO-ROWED BARLEYS (CAN. GOLDTHORPE, CHEVALLER)

No variety given. Argentine, Gaza, Danubian (with *H. distichum*).

H. hexastichum var. *parallelum*. Brewing Chilean (also *vulgare*). var. *pyramidatum* Persian, Beyrout (*vulgare* and *distichum* in both).

H. distichum. Californian and Chilean Chevallier (with some *vulgare*), Tripoli Ouchak type, Ouchak (mixed with *vulgare*).

Density is rejected as a major distinction for sub-species in some later classifications on account of the gradations which occur. These are illustrated in Fig. 21 by ears of a Manchuria and three Californian barleys, Coast, Atlas and Club Mariout, of which the first three might be included in Beaven's narrow-eared *vulgare*, while the Mariout is considerably wider, though it would hardly be considered as *hexastichum*. In extreme wide-eared forms the ear is pyramidal, as shown in Fig. 18. Harlan⁸ classifies barleys in four species based on fertility, as follows :—

Species in Harlan's Classification

Six-rowed barleys. *H. vulgare*, all florets awned or hooded.

H. intermedium, laterals bear neither awns nor hoods and their kernels are much reduced in size.

Two-rowed barleys. *H. distichon*, lateral spikelets infertile but with rudimentary, non-functioning sexual organs.

H. deficiens, lateral spikelets greatly reduced with no sexual organs.

Of these only *H. vulgare* and *distichon* need be considered as malting barleys. *H. intermedium* is rare and possibly only consists of hybrids. *H. deficiens* is only represented by some Abyssinian and Asia Minor barleys. Each of the species is divided in eight varieties, with what are considered major variations. They are first separated into hulled and naked varieties, each of which is differentiated according as it is awned or hooded. The four groups so obtained are further sub-divided into two varieties according to the colour of the kernels; white, blue or purple on the one hand and black on the other. Each of these eight varieties is then divided according to minor characters into sub-varieties, first by the width of the outer glumes, then by the colour of the kernels and structure of the awns, and finally, where possible, into narrow-eared, wide- and very wide-eared sub-varieties. Most of the barleys generally met with would fall into one or other of the following sub-species :

H. vulgare, sub-var. *typica*—six-rowed, awned, white kernels, lax.
sub-var. *pyramidatum*—six-rowed, awned, white kernels, dense.

sub-var. *cærulescens*—six-rowed, awned, blue kernels.

sub-var. *nigrum*—six-rowed, awned, black kernels.

H. distichum, sub-var. *nutans*—two-rowed, hulled, awned, white, lax.

sub-var. *erectum*—two-rowed, hulled, awned, white, dense.

sub-var. *nigricans*—two-rowed, black kernels.

Beaven disputed the value of colour as a varietal distinction, but Coast and several strains of Manchuria would be included in Harlan's sub-variety *cærulescens*.

R. G. Wiggins⁹ agrees in dividing cultivated barleys in four species, *H. vulgare* with 29 varieties, *H. intermedium* with 3 varieties, *H. distichon* with 20 varieties, and *H. deficiens* with 8 varieties. The characters used to distinguish varieties in the large groups are the same as those of Beaven's classification, with the addition of habit of early growth. Sub-varieties or strains are distinguished by attitude of spike, differences in dates of emergence and maturity, with characters of outer glumes, grain, foliage, culm, rachis, head and productivity. Some of the well-known six-rowed varieties would be classified as follows :—*H. vulgare*. Lemmas awned, kernels white, blue or purple.

(1) Narrow-eared, nodding barleys—

(a) Rachilla—long, straight hairs. Manchuria selection.

(b) „ —short, fine hairs.

(1) Kernels medium to small, Manchuria, Oderbrucker,
under 1 cm. O.A.C.21.

(2) Kernels long and coarse, Coast, Mariout.
over 1 cm.

(2) Wide-eared barleys—

(a) Rachilla—long straight hairs. Winter Club.

(b) „ —short, fine hairs. Chilean.

(18) Summary.

The axis of the spike of barley is jointed and bears three florets at each node alternately on either side along its length. In six-rowed barleys all three florets are fertile, in two-rowed the medium floret at each node only is fertile and produces a corn. The distance between each node varies in length. When it is comparatively great the corns can lie closely to the axis and produce narrow-eared barleys. When the internodes are short the corns must lie at a wide angle from the axis and the barley is wide-eared. Fertility and density are the main characteristics on which Beaven's classification is devised. This classification is generally used in England, but there is such a gradation of width that density is rejected as a major varietal

STRUCTURE AND CLASSIFICATION OF BARLEY § 18

distinction in Harlan's classification which is used in America. Most English and European malting barleys are two-rowed, Spratt-Archer and Chevallier being typical narrow-eared, while Plumage-Archer and Goldthorpe are characteristic wide-eared varieties. Classifications based on morphology are becoming increasingly difficult to make use of, on account of the increase in the number of hybrid barleys.

The barley corn represents both the fruit and seed of most other plants. The fruit, derived from the ovary of the flower, is reduced to a very thin skin covering the seed proper, which is produced from the ovule. The husk does not actually belong to the fruit, but is part of the leaf system of the plant. The embryo is the living part of the seed, taking its nourishment saprophytically from the endosperm, which is a storehouse of starch, protein and other nutrient materials. It secretes enzymes for this purpose from the epithelial layer and absorbs the liquefied products of digestion through the same layer for the developing embryo and rootlets.

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CHAPTER III

MALTING BARLEYS

BRITISH BARLEYS

(19) Older Varieties.

Both six-rowed and two-rowed barleys are grown in the British Isles and were described by writers of the sixteenth and eighteenth centuries, but little of the former attains sufficient perfection to make it attractive to maltsters and it is almost entirely used for feeding purposes. It seems probable that the early Celtic barley was six-rowed. It gave its name "bere" or "beere" to a great number of place names and probably to beer itself. The name has been perpetuated for barley in Scotland, together with "bigg," which was apparently introduced from Iceland. The narrow-eared kind, *H. vulgare*, can be grown on poorer soils and at higher altitudes than most others. The wide-eared *H. hexastichum* is also grown to some extent as a winter barley. The possibility of increased yields and winter hardiness has led to attempts to find improved strains of six-rowed barleys and some have been used with a measure of success in brewing. Among these is a winter-hardy, but not very agriculturally successful, selection of *H. hexastichum* made by Dr. E. S. Beaven and referred to as F 112, and B 244 raised by Engledow at Cambridge.

It would appear that Spratt and Archer are modern representatives of the original two-rowed types. The wide-eared Spratt has now gone out of cultivation, but it has left its name in conjunction with that of Archer in one of the best modern hybrids. At the close of the first quarter of the nineteenth century the Rev. John Chevallier was attracted by the fine appearance of a few ears of barley that had grown from seed scattered by a labourer in his garden at Debenham, Suffolk. These were cultivated and became the parent stock of Chevallier, which was a fine malting barley and became very popular among brewers, though it is now hardly ever met with in England, having been replaced by more prolific races with stiffer straw. It is narrow-eared, nodding or bending over when ripe, with moderate-sized, shapely, plump grain. The rachilla or basal bristle can be dis-

tinguished from that of all other English barleys on account of its length and short, downy hairs. Since Chevallier has practically gone out of cultivation in England, on account of its weakness of straw, almost any two-rowed barley with this type of basal bristle can be assumed to be imported, possibly from Australia. Many selections have been made from the original Chevallier or allied barleys, such as Archer, among which are Hallett's Pedigree, Webb's Kinver and Prior's Chevallier, of which the last is largely grown in Australia.

Another famous barley, the Goldthorpe, originated in 1889 from a selection from a field of Chevallier at Goldthorpe in Yorkshire. These two strains were typical of narrow-eared and wide-eared barleys respectively, and barleys were formerly generally referred to as of Chevallier or Goldthorpe type according as they were narrow- or wide-eared. Spratt-Archer and Plumage-Archer, which have, in most districts, replaced them but resemble one or the other very closely in appearance of ear, are now more usually taken as representative of the two types.

(20) Selection and Hybridisation.

Most of the strains of barley cultivated in the more advanced agricultural countries have arisen from seed derived from selected ears of older and generally mixed barleys, or, more recently, by hybridisation designed to combine the desirable qualities of two selected parents. Hybridisation is carried out by removing the unripe anthers of one plant and dropping a ripe anther from the flower of another on the exposed stigmas. Fertilisation brought about in this way results in the production of hybrid seed, referred to as the F₁ generation, which has the dominant characteristics of the parents. When a pair of characters only are combined in the hybrid, such as wide-ear and narrow-ear, the plants of the F₂ generation from the F₁ seed, according to Mendel's Law, would vary in such a way that one-quarter of them would breed true in the F₃ and successive generations with the dominant character of the original parents, another quarter with what is known as the recessive character, while the remaining half would resemble the hybrids of the F₂ generation. This is exemplified for wide- and narrow-ears in Spratt-Archer, described in Section 22. Other characters, e.g., stiff and weak straw, would usually also be involved and the results of hybridisation would be much more complex.

Among the properties which may be sought in the progeny or thought desirable to impress on a race not already possessing them are stiffness of straw to prevent lodging, disease resistance, early ripening, colour, winter hardiness and malting quality,

which usually means low nitrogen content. A basic principle is that the two truly breeding strains of the F₂ generation will each produce the same kind of barley as long as it is grown, since cross fertilisation only occurs very exceptionally in nature, as shown by the maintained individuality of the several hundred varieties grown side by side for many years in Dr. Beaven's barley nursery at Warminster.

Hybridisation by artificial cross-fertilisation has been an outstanding success in Great Britain and Ireland, where probably 75% of the barley grown consists of Plumage-Archer and Spratt-Archer. The time is, perhaps, not far distant when the entire acreage in most countries of Europe and North America will be sown with pure line races. These must vary to a certain extent, even in the comparatively small area of England, to suit different climatic and soil conditions, but it is to the brewer's advantage that the number of races should be restricted as much as possible to avoid mixtures in bulks. Uniformity is one of the most important qualities of malting barley and this is best secured by selection of single plants from an old variety composed of individuals which, although more or less alike in appearance, differ in various inheritable characters. Beaven² states that the same uniformity is never obtained in the aggregates composing hybrid races but greater productivity and better quality can be secured by hybridisation.

(21) Plumage-Archer and Wide-eared Barleys.

Plumage-Archer was produced by E. S. Beaven in 1905 by crossing selected strains of Plumage and Archer in the manner described. Plumage is a wide-eared variety introduced from Denmark in 1902 by Beaven, who selected and cultivated a pure line from it. The straw and neck are long and, like Goldthorpe, it is liable to loss of ears when ripe. It ripens early, giving grain of yellow colour and good malting quality. Archer is a narrow-eared variety but lies between Goldthorpe and Chevallier in density of ear. The grain is comparatively small, of greyish colour with finely wrinkled skin and good malting quality. It is moreover characterised by short, stiff and erect straw and gives a high yield. The rachilla is short and covered with long hairs. Beaven combined the stiff straw of the narrow-eared Archer with the large grain of the wide-eared Plumage and selected from the progeny a wide-eared strain, characterised by high yield and grain of low nitrogen content. This he called Plumage-Archer of which pure races have continually been selected and distributed from the original strain.

The wide-eared barleys, Plumage, Goldthorpe, Standwell,



FIG. 20
PLI MAGE-ARCHER AND SPRATT-ARCHER BARLEYS

Facing page 33

Burton Malting and Golden Pheasant, are grown to a limited extent, but most of the older strains, such as Invincible, Brewers' Favourite, The Maltster, Golden Melon and English Binder, have become extinct or almost disappeared since Plumage-Archer proved its superiority under most climatic conditions. English Binder was distinct from and must not be confused with the narrow-eared Binder grown largely in Denmark, Poland and Sweden. Standwell was among the earliest of the hybrids and was produced by Messrs. Garton from Chevallier and Fan. These wide-eared barleys displaced the narrow-eared races in Southern Scotland and the northern counties of England, to be ousted in their turn in Berwickshire and the Lothians by Plumage-Archer, while Plumage has largely displaced the other wide-eared varieties on the Yorkshire Wolds in the East Riding. A serious defect of Standwell, Goldthorpe and Plumage is the liability of the heads to break off when approaching ripeness, on which account they were often harvested before they were ripe. This does not seem so serious with Standwell as with most barleys, since it appears to mature successfully in stack, but it gives many blind corns in the ear, reducing the yield.

(22) Spratt-Archer and Narrow-eared Races.

Spratt-Archer was produced by H. Hunter in Ireland in 1908 by hybridisation of Irish Archer 1, a pure line selection of Archer originating in Eastern England, with Spratt. The latter is a very dense-eared variety with ears borne stiffly erect. Its grain is large and greyish in colour. These two barleys were cross-fertilised in 1908. The F1 generation of 1909 was narrow-eared with fairly long straw, both of these being dominant characteristics. The F2 generation of 1910 contained narrow- and wide-eared plants in the proportion of 36 to 10. In the F3 generation of 1911, 11 of the 36 narrow-eared plants remained narrow-eared, the remainder produced both narrow- and wide-eared progeny. The 10 wide-eared F2 plants bred true in the F3 generation. The strain finally selected after trials for yield, malting quality and low nitrogen content was the narrow-eared race called Spratt-Archer. This was introduced for trial in Norfolk in 1920 and distributed throughout the country in 1922.

The grain of Spratt-Archer is typically rounder than the rather large Plumage-Archer, which tends to be more spindle-shaped. In comparative trials spread over several years at Warminster, Beaven found that it gave on the average a slightly higher yield and nitrogen content than Plumage-Archer. There is little difference in the average bushel weight of these or other British barleys. The range may be placed at from 50 to 60 lb., with an

average of 54 lb. The bushel measure is now rarely used, barley being sold by weight on the accepted basis of 56 lb. to the bushel or 448 lb. to the quarter. The 1,000-corn weight is a very useful indication of grain size. It usually ranges between 36 and 42 grams for moisture-free English barleys. Very thin corns may weigh 30 grams and very bold barleys 48 grams per 1,000 corns.

Among other narrow-eared races of which considerable quantities are grown are New Cross and Fortyfold, while a few Continental strains are also occasionally grown, among them Opal, Continental Binder, Swedish Gold and Princess. A small quantity of the last was grown in Essex a few years ago and during damp weather produced some very fine samples, but it is apparently not suited to dry seasons and has been eliminated. Two hybrids of Spratt-Archer and Plumage-Archer have recently been liberated by Beaven and come into cultivation. Of these Golden-Archer is a mass selection and 35/51 a single plant culture. They are both narrow-eared barleys, characterised by an attractive colour.

(23) Barley Types and Districts.

The average characters of a race or variety of barley remain constant on account of the self-fertilisation which almost invariably occurs, but the external appearance of the grain and its malting quality vary very much from place to place, giving rise to characteristic "types." The influence of soil and season on both quality and appearance is very great, and, in many cases, barleys of different allied races may approximate more closely to a single type than would barleys of the same race grown in different districts and would malt more regularly if bulked together. The type is thus only due in part to variety and barleys of different races are modified by the local cultural conditions until they approximate closely to each other, and more homogeneous, better malting bulks are often secured on the basis of type than would be obtained by mixing grain of the same strain grown in different places and probably unevenly matured. Barleys from different districts have well-marked characteristics which persist from year to year, though modified to a greater or less extent by weather conditions. These variations in character, based primarily on the variety best adapted to the locality, are due to the nature of the soil, climatic conditions, elevation, nearness to the sea, etc. As a result, British barleys are generally described by the name of the county or district of origin and, when possible, by the variety.

Fineness of skin and relatively small berry are typical of Norfolk barley at its best, but it may suffer greatly in dry seasons

owing to the shallowness of the soil, in some places no more than a few inches deep. Spratt-Archer is better suited to light lands than is Plumage-Archer and is consequently the variety mainly grown in Norfolk, Plumage-Archer gradually displacing it as the soil becomes heavier through Suffolk down to Essex, where the latter variety predominates, though the finest quality of autumn-sown Spratt-Archer is grown in the last county when the weather is suitable. When winter climatic conditions are favourable, the finest barleys of the season are frequently found among the autumn-sown grain, either Plumage-Archer or Spratt-Archer, but mainly the former. All other conditions being equal, barley grown on land with limestone subsoil is to be preferred and the quality is generally best when it is subject to the mellowing effect of sea mists. The limestone barleys often give better results than the appearance of the grain suggests, whereas barley grown on strong lands, and on some light soils, is apt to be deceptive in giving worse malts than would be anticipated. The predominant variety in each district depends largely on the nature of the soil but seasonal influences may ultimately prove the deciding factor and Spratt-Archer may do better on heavy lands than Plumage-Archer in very dry seasons. The Spratt-Archer is, on the other hand, more liable to lodge when the growth is heavy than the stronger strawed Plumage-Archer.

In Lincolnshire the best barley land is that of the limestone of Lincoln Heath and Lincoln Cliff, a narrow tableland running right through the county from north to south, where Spratt-Archer is mainly grown. The Wolds also have a chalk subsoil with perhaps a foot of soil on the best lands where fine barley is grown. There are tracts of clay in the vales below the high lands where good barley is occasionally grown in dry seasons. The Fens never grew barley fit for malting until the hybrids were introduced and immediately before the War a fair amount of Standwell or similar hybrid barley was grown and, in some years, was suitable for making common mild ale malt. It always contained a high percentage of nitrogen and gave highly diastatic malt suitable for malt extract manufacture. Prior to this Spratt was a favourite in the district. It was an ugly barley which yielded well and had a stiff straw. Practically no barley is now grown in the Fens as more paying crops, particularly sugar beet, have replaced it. The rich soil is typically suited to quantity with high nitrogen content rather than quality.

In Yorkshire a different type of barley is grown, a larger, rather coarser grain than that of the south-eastern districts being typical. Owing to the late harvest of the higher districts it may be very weathered or fail to ripen properly but in favourable

seasons good quality barley is obtained. Plumage-Archer is not very successful north of the Trent until the southern Scottish counties are reached, where some very fine barleys are raised. It tends to a greyness of skin which was characteristic of Archer when grown in the northern counties years ago. It has, however, been grown in increasing quantities in some suitable districts in Yorkshire. Plumage appears to be the most successful of all the wide-eared barleys north of the Trent. It is better in quality and yield than Goldthorpe, sharing with the latter a bright gold tint which will withstand bad weather conditions. Fine Plumage-Archer barleys are grown in the south-west of England, particularly in Somerset, where they are large berried but of finer texture than those grown further north. Some of the barleys grown in the south-eastern counties may be compared with them, Kent producing some very fine grain.

(24) Varietal Characteristics.

The finer varietal characteristics can only be ascertained by comparative trials under varying conditions at different places over a number of years, such as those carried out by the National Institute of Agricultural Botany of Cambridge. Some of these are shown by yield, appearance and market price but the typical properties of the varieties, found by averaging a large number of trials, are very liable to be altered by external conditions so that growers are guided by results in their own districts and may produce better malting barley from varieties that would elsewhere be regarded as inferior to some others. In each variety there appears to be a tendency to a composition peculiar to itself but this varies within a considerable range and the effects of soil and season are so great as to over-ride varietal influences.

Among the varietal differences or tendencies of most importance to brewers which have been detected in these trials³ are the nitrogen content of the barleys, the extracts given by malts from barleys of the same nitrogen content and the nitrogen content of the wort produced from the malts. For example, Plumage-Archer, Spratt-Archer and their hybrids Golden Archer and 35/51 have on the average a lower nitrogen content and higher extract than Archer or Chevallier. Standwell, which is not a favourite on account of its low and variable yield, is of interest because it usually gives a higher extract than Plumage-Archer at any given nitrogen content. This is because it modifies easily on the malting floor, for which reason it gives an exceptionally high permanently soluble nitrogen in the wort. Kenia and Isaria when grown in England contrast with this in giving lower permanently soluble nitrogen for the same barley nitrogen content.

FOREIGN TWO-ROWED BARLEYS

(25) German and Czecho-Slovakian Barleys—Hanna Strains.

The *Landegerste* or local barley of some districts has in course of time become so homogeneous and characteristic of the locality, through the operation of various processes of natural and agricultural selection by which the best types have survived, that it has served as an excellent starting point for selected races. This applied with special force to the hardy, bold, early ripening barley of Moravia from which a number of pure line strains of "Hanna," usually distinguished by the name of the originator, have been derived. These narrow-eared *nutans* races have of recent years provided a very large proportion of the best European brewing barleys.

The original pure line Hanna was selected and improved by Dr. E. von Proskowetz at Kwassitz in the 80's of the last century. Among other races for which the same name is used are Heine's Hanna selected in Saxony in 1890, numerous strains of Bethge's Hanna of Bohemian descent, of which Viktoria was originally a stiff-strawed strain of Bethge XI with an ear midway between *erectum* and *nutans*, while Bethge's Hanna XIII is an early-ripening *nutans* strain of Viktoria. Hado was a strain of a Moravian Hanna and crossed with Eglfing of Upper Bavaria in 1917, gave the medium early Eglfing-Hado barley. Many of the most widely grown barleys in Czecho-Slovakia are Hanna selections, among them being Selecta Hanak 1, Hanak 2 and Hanna Kargyn.

Bavaria and Danubia are two well-known selections, by Ackermann, from Middle Bavarian *Landegerste*. Bavaria being more suited to heavy lands and Danubia for light and medium soils, they were crossed in 1914, giving Isaria which was distributed in 1924.

The barleys imported into England come mainly from Moravia, Bohemia and Slovakia but it is only rarely that the strain is known to importers. In a good season, barleys from the best districts in Moravia are probably the finest two-rowed barleys in the world. They are of bold well-filled type and usually somewhat higher in nitrogen content than the best quality English barley. Some brewers like a proportion with English malts in the grists, finding that they are helpful in yeast nutrition and development. The Bohemian barleys are also of a bold well-filled type but usually not quite so fine in quality and coarser in skin than Moravian. The Slovakian barleys are generally smaller and rather elongated in shape, whiter in colour and more steely. They are mostly of

the older Hanna strains. The quantity imported is now greatly restricted by the "gentleman's agreement" of 1935 to limit the quantity of foreign barley in British beers, six-rowed barleys being generally preferred to supply the 15% usually considered necessary.

(26) Scandinavian Barleys.

Brewers and farmers are immensely indebted for improved races of barley to the plant breeding stations at Svalof in Sweden⁴ and Abed in Denmark, the names of N. Hjalmar-Nilsson and H. Nilsson-Ehle of Sweden being particularly associated with the production of pure line selections and breeding for special characteristics by cross-fertilisation respectively. Among the best known Svalof selections are Gull or Gold, derived from the old mixed barley of Gothland; Hannchen from Bohemian Hanna; Chevallier 2 and Brage from English Chevallier and Princess from English Prentice, while Seges (Victory) was the result of a cross between the first two and Princess 2 was derived from Princess and Chevallier 2. These are all narrow-eared, two-rowed barleys but they can be divided into two groups.⁸ The first, to which Chevallier 2 and Princess belong, comprised late-ripening, weak-strawed barleys which lodge in wet weather, particularly if heavily manured, and give smaller crops. These barleys were consequently not liked by farmers although they modified readily and gave good brewing malts. Barleys of the second group are stiff-strawed, early-ripening, yield better and are consequently preferred by farmers. Gold, the predominant variety in Sweden from 1880 until the earlier years of this century, belonged to this group and gave good crops, since its short, stiff straw made it capable of standing up to nitrogenous manure.

The best known Danish barleys are Binder, a selection from Bohemian Hanna, Opal, Kenia and, very recently, Maja, all obtained by crossing Gold with Binder. A selection of the Abed Opal was made at Svalof and is known as Opal B. All these barleys belong to the early, stiff-strawed group and have proved good malting and brewing races. Binder not only yielded better than Gold but had the good brewing qualities of the weak-strawed varieties. Hence its great popularity and the reason for its becoming the predominant kind in Sweden by 1930. Opal and Kenia are as easily modified as Binder on the malting floor, give higher extracts and, with this, combine fine agricultural and brewing qualities. Kenia has the stiffest straw and is the earliest to ripen of those yet mentioned. Opal was rather uneven but the pure line selection Opal B, made at Svalof in co-operation with the

Stockholm breweries after stocking malting trials to pick the best from 10 pure lines, has been very successful. Maja is apparently equal in malting quality to Kenia and Opal B and superior to both in straw stiffness. Kenia and Maja are now very widely grown in Sweden, while Ackermann's Isaria has been introduced from Germany.

Malting barleys are imported into England from Denmark but the quality is generally much inferior to that received from Czecho-Slovakia, though in good seasons they are rather similar to English Eastern Counties grain. The Polish barleys are of somewhat similar type but larger and thinner than the Danish. Of recent years a good deal has been done to improve French barleys but little is seen in this country, although 40 years ago large quantities were imported from the Champagne districts and known in the trade as Saumur and Sablé barleys.

(27) Other Two-rowed Barleys.

Two-rowed barleys are also shipped from South Australia, Victoria and New South Wales, under the name of Australian Chevallier or Prior, but they are not very popular with British brewers, partly because they arrive too late for malting and are liable to decrease in germinative activity if held over, partly on account of the irregularity of the shipments and partly because they tend to be steely and difficult to modify, with danger of mould on the floors on account of damage to their delicate skins. Fine samples of Chevallier barley are also obtainable from Chile. In good seasons this is a bold sunny barley, making very good malt. Barley of similar type was formerly imported from California, but is now rarely if ever grown. Two-rowed barleys have not been so generally successful in America as the six-rowed. Hannchen, imported from Svalof in Sweden, has the widest range, more than three-quarters of it being grown in Oregon. It has replaced the original Californian Chevallier and is grown under irrigation in the Klamath Falls district of North California and South Oregon, in Washington, and, to a smaller extent, in Idaho. Horn is a selection made in 1909 by Harlan from an Austrian barley and mainly grown in the dry lands of Wyoming and Montana. White Smyrna is another two-rowed race grown fairly extensively in South Dakota and Colorado. It is a selection from a Smyrna barley. The smooth-awned Spartan is a two-rowed hybrid between Michigan Black Barbless, selected at the Michigan Station from Lion and crossed with a hybrid two-rowed barley.

The two-rowed Ouchak barleys from Anatolia and Syria, sometimes containing black corns as well as white, are often useful

brewing material but they do not malt very readily and give extracts that are rather disappointing for malts that may be about the same size as English. The two districts of Hama and Homs in North Syria produce two-rowed barleys which are considerably smaller and generally thin but may malt well and give good malt, though the extract is low. They may contain 5–10% of black grain and some reddish, rounded knobs of clay, which are difficult to screen out.

SIX-ROWED BARLEYS

(28) Mediterranean and Manchuria Types.

It is generally impossible to differentiate imported six-rowed barleys as botanical varieties, apart from the distinction between narrow- and wide-eared kinds and even this is difficult on account of gradations in density. Differences associated with the country of origin are much greater than those due to variety, and it is under the name of the country or port from which they were shipped that these barleys are best known. Two groups of very distinctive appearance and brewing qualities may, however, be differentiated in the narrow-eared varieties, and are usually referred to as Mediterranean and Manchuria type barleys. The former includes the barleys of the Mediterranean basin, Spain, North Africa, Asia Minor, some Eastern European districts and barleys originally derived from North Africa which are now grown in California and Chile. The Manchuria group includes the majority of the malting barleys of the United States east of the Rockies and of Canada, with allied barleys in Central and Eastern Europe and Asia from whence they were probably derived. Both these groups might be included in the same botanical variety, *H. vulgare*, but they are so different in composition and brewing qualities as to make it clear that classification on other than morphological features is essential for brewing purposes. Wide-eared, six-rowed barleys accompany the narrow-eared Mediterranean types but are not so sharply differentiated from the latter in brewing qualities as are the American barleys of Manchuria type. The barleys obtainable on the market under the name of their country of origin are remarkably uniform in type, much more so than they would be if attempts were made to bulk them according to varieties, regardless of local variations. The trade in barley from exporting countries is greatly affected by local requirements, political and financial conditions. At the present time California provides the largest quantity of imported barley on the English market and this gives very satisfactory malt.

(29) Characteristics of Six-rowed Barleys.

The criteria for judging six-rowed barleys seem to be different³ from those applied to two-rowed barleys, since the advantages usually claimed for them are for drainage material in the mash tun and for "sun." The latter probably means good and constant germination, resulting from good harvest weather. Though the extracts of six-rowed malts are lower than those of two-rowed, the former show to advantage when the extract obtained is calculated back to barley bought, on account of their lower moisture content. Thus 448 lb. of barley containing 18% of moisture would yield 338 lb. of dry malt if the malting loss was 8% on dry barley, while another containing 11% moisture would yield 366.8 lb. of dry malt if the loss were the same. If 336 lb. of dry malt from the former yielded 100 lb. of extract, the 448 lb. of original barley would yield 100.6 lb. This would be obtained from 448 lb. of the latter barley if the extract of its malt was 92.1 lb. on dry matter.

Another important feature of six-rowed malts, which will be discussed in later chapters, is the comparatively low soluble nitrogen percentage on wort solids. The practice of blending six-rowed malts from English and foreign six-rowed barleys of Californian or Mediterranean type is justified if the object is to obtain a low ratio of wort nitrogen to wort solids but if a higher wort nitrogen is required to obtain sufficient yeast crops with low gravity beers, the Manchuria type of barley as grown in America would apparently be more suitable.

(30) American Brewing Barleys.

Six-rowed barleys have always predominated in America and are divided in the two general groups, Manchuria and Mediterranean. The Manchuria barleys are preferred by American brewers, who use them almost exclusively and have adapted their malting and brewing processes to this type which is most extensively grown east of the Rockies. The corns are considerably smaller than those of the Mediterranean type barleys and the nitrogen content higher. Although this may amount to 2.0 or 2.5% on dry weight, the barleys ripen well and malt easily. Most of the acreage in the United States is now being sown to varieties recently developed there or imported by plant breeders. (H. V. Harlan and M. L. Martini.⁶)

(31) Manchuria and Oderbrucker Barleys.

Manchuria was apparently first imported in 1861 from Germany, and was later grown under such names as *Manshury* and *Mensury*,

while the Ontario Agricultural College imported a very similar barley in 1881, which it distributed as *Mandscheuri*. It is an early ripening, vigorous barley from which many valuable strains with blue or white kernels have been selected. It is characterised by rather small corns, with thousand-corn dry weight averaging 28 to 35 grams and high nitrogen content, usually about 2% on dry weight. *Minnesota* 184, derived from the Ontario *Mandscheuri*, is the most widely grown selection.

Oderbrucker was originally identical with or similar to *Manchuria* and existed in a number of blue and white strains. As known to-day it is a six-rowed, rough-awned barley with white kernels. It came from the valley of the Oder in Germany about 1865. In 1889, the Ontario Agricultural College received a new supply from Germany and sent it to the Wisconsin Experiment Station, whence the selections *Wisconsin Pedigree* 5 and 6 were liberated in 1908 and now constitute the entire *Oderbrucker* acreage, yielding very good malting barley.

Odessa, an importation from South Russia, is similar to *Manchuria* in many ways and even more tolerant to summer heat and drought. The *Manchuria*, *Oderbrucker*, *O.A.C.21*, a Canadian selection of *Manchuria*, and *Odessa* are all grown in the northern States, east of the Missouri River, but the centres of production are different. *Odessa* is largely confined to South Dakota. *Oderbrucker* is grown most extensively in Wisconsin, Illinois and adjacent areas of Minnesota and Iowa. *Manchuria* is grown more commonly in Western Minnesota and North Dakota, while *O.A.C.21* is the leading Canadian barley.

Trebi, the most extensively grown barley in America, is not, as usually grown, a malting barley but is used for feed. It was isolated in 1909 by Harlan from a barley originating to the south of the Black Sea near Trebizond and released in 1918. It is a six-rowed, rough-awned barley with large blue kernels, more closely allied to the Californian types than to the Manchurian and appreciated by farmers on account of its high yields.

(32) Smooth-awned Barleys.

Curiously enough the first real contribution to barley breeding in America was accomplished by hybridisation rather than by selection. This was *Horsford*, produced in 1879 by crossing *Nepal* on one of the common six-rowed awned barleys of the eastern States. It was named after its breeder and is a hooded, six-rowed barley. (See Fig. 10.) The hooded barleys are a response to the farmers' dislike of rough-awned barleys and most of them, among which are *Beardless* and *Success*, are derived from *Nepal*.

More recently smooth-awned barleys which do not shatter so badly as the hooded types have been developed, almost entirely from *Lion*, a smooth-awned black barley, introduced from Russia in 1911. These have been crossed on Manchuria barleys giving some good malting barleys, such as *Velvet* and *Glabron*, produced by co-operation between the Minnesota Agricultural Experiment Station and the U.S. Department of Agriculture and released in 1926 and 1929. *Hero* and *Vaughn* are other smooth-awned barleys derived from *Lion* and *Club Mariout*. *Wisconsin Pedigree 37* and *38* are good malting barleys produced by the Wisconsin Agricultural Research Station from an Oderbrucker selection, *Wisconsin 5*, by crossing with *Lion* and released in 1929 and 1930. The two-rowed smooth-awned *Spartan* was previously mentioned.

It is interesting to note that smooth-awned barleys are at a disadvantage in districts where part of the crop is derived from self-sown corns from the previous harvest. The barbs, when still attached, cause the "shattered" corns to penetrate 2 inches into the soil and produce what is known in California as a "volunteer crop."

(33) Californian Barleys.

The six-rowed barleys of the Pacific Coast States belong mainly to what has been called the Coast or Mediterranean type to indicate their place of origin, or distinguish them from the Manchuria barleys. During recent years their cultivation has been well organised and much has been done to improve their quality. (G. A. Wiebe.⁶) The barley known as Coast was introduced into California about 1770 by the early Spanish Missionaries from Mexico and no doubt came from Spain and originally from North Africa. In recent years the very mixed grain included under this name has been displaced by selections made by H. V. Harlan and V. H. Florell in the co-operative work of the United States Department of Agriculture and the University of California. Among these selections the best known and most widely cultivated strain is *Atlas*, which was distributed from Davis, California in 1924. Other selections are known as *Coast* and *Californian Tennessee Winter*—the latter is not to be confused with the most widely grown American Winter Barley with the same name which is very similar to Manchuria and believed to have originated in Switzerland or the Balkans.

These are all six-rowed, narrow-eared barleys with considerably larger grain than Manchuria; thousand-corn weight between 36 and 42 grams for grain of good size and bushel weights of 48–54 lb. The new selections differ from the original Coast in earlier

ripening, increased yield, stiffer straw and greater regularity with better appearance, but they are so closely allied that varietal differences are largely obliterated by the influence of soil and season. In general they are plumper and less husky than the old barleys and show less colour. Colour does not, however, serve to distinguish the strains when grown in different localities as it depends to a great extent on the conditions of growth, but when grown together there is a greater tendency to blue colour in the Coast, less in the Tennessee Winter and least in the Atlas.

The result of their cultivation and changes in the location of the barley-growing districts has been the production of finer skinned grain, yielding an extract of 96 and even 98 lb. per quarter of dry malt, or 77-78%, in comparison with the 89-95 lb. per quarter or 71-76% on dry malt which was formerly more usual. They also usually have a lower nitrogen content and enzymic activity, for which reason some brewers still prefer the old Coast or Bay Brewing barley, as it was generally known on the English market where the barleys are often distinguished as of "Atlas type" and "Coast type."

Photographs of ears of two of the new selections, Atlas and Coast, from Wiebe's paper, together with ears of Manchuria and Club Mariout are given in Fig. 21. These show a gradual increase in the width of the ear from the Manchuria to the Coast, Atlas and Club Mariout, indicating that this characteristic is not altogether satisfactory for purposes of classification or differentiation of varieties.

(34) Mariout Barleys.

Several wide-eared barleys have also been introduced into California and are widely grown. Some of these have proved suitable for cultivation in very dry districts. *Club Mariout* is a moderately wide-eared barley with large corns which sometimes appear golden yellow through the thick husk. It was introduced by the United States Department of Agriculture from the irrigated district of Lower Egypt in 1903. It is a rough-awned variety with a very short-haired rachilla and came into cultivation in California between 1919 and 1921, where it is appreciated on account of the short time between planting and maturity, which permits last seeding, and also because it does well with small rainfall. *California Mariout* is a rough-awned, blue kernel barley, with long-haired rachilla. It was obtained through E. Clemens Horst from the dry hill region west of Lake Mariout in Egypt in 1905. It was grown rather widely in 1918-1920 but there is little now in cultivation. Hero and Vaughn, of which photographs are given in Figs. 9 and



FIG. 21

SIX-ROWED AMERICAN BARLEYS (MANCHURIA, COAST. ATLAS, CLUB MARIOUT)

[Facing page 44]

12, are smooth-awned crosses from Lion and Club Mariout. They are not good malting barleys, though their appearance is often attractive.

The wider-eared Californian barleys, usually referred to as of Mariout type, are characteristically more difficult to malt than the narrow-eared races and, when insufficiently modified, are liable to give rise to serious trouble with sediments or turbidity in the beer. When adequately malted, however, they yield good brewing material, often giving greater diastatic activity than the other strains, but they have not generally been received with as much appreciation in breweries as the narrow-eared barleys. The husk of Vaughn is delicate and very liable to fray when malting.

(35) Grading of American Malting Barley.

Official grain standards have been set up by the United States Ministry of Agriculture to facilitate merchandising of barley as between country and terminal elevators and purchaser and now include grades which shall conform closely to maltsters' requirements and guarantee contract by grade deliveries of barley suitable for malting. As amended effective on July 1st, 1935, they divide barley into four classes: Class 1—Barley; Class 2—Black barley; Class 3—Western barley and Class 4—Mixed barley. Class 1 includes all white barley grown east of the Rocky mountains and may include not more than 10% of barley of other classes. It is divided in Sub-class A—Malting barley and Sub-class B—Barley for other purposes.

Malting barley (Class 1, Sub-class A) is defined as six-rowed barley of Class 1, which meets the requirements of grades 1 to 3 and which, after removal of dockage, contains not more than 5% of two-rowed and/or other types or varieties of barley of unsuitable malting type such as Trebi and Black; which contains not more than 15% of barley and other matter that will pass through a 20-gauge metal sieve, with slotted perforations 0.076 of an inch wide and $\frac{1}{4}$ of an inch long; which contains not more than 4% of damaged barley; and shall not include bleached barley. Barley of this sub-class shall contain 75% or more of mellow barley kernels which kernels are not, *en masse*, semi-steely.

The sub-class is then divided into 5 grades, of which the first three include the malting barleys and a "sample grade" for barley which contains more than 16% of moisture or which is in some other way too low in quality for inclusion in the grades. Barley which is badly stained or materially weathered cannot be graded higher than 4. The grade requirements are given in Table 1.

TABLE 1.—GRADE REQUIREMENTS FOR AMERICAN BARLEYS, CLASS 1

Grade	Minimum limits of		Maximum limits of			
	Bushel* weight lb.	Sound barley %	Heat damaged %	Foreign material %	Broken kernels %	Black barley %
1	47	95	0.1	1	4	0.5
2	46	93	0.2	2	8	1.0
3	43	90	0.5	3	12	2.0
4	40	80	1.0	4	20	5.0
5	35	70	3.0	6	30	10.0

(36) No. 1 Standard Californian Barley.

It is always desirable that malting barley should be bought on sample but to facilitate sales abroad an "Official No. 1 Standard Californian barley sample" is made up about the end of August or early September by the San Francisco Exchange from individual sacks collected from every part of the State. These are examined and the best and worst rejected so that the remainder shall form a "Fair average Standard of the crop." This sample is then screened and the impurities ascertained and an exact quantity of the impurities returned to each individual official sample on which contracts may be based. The barley thus sold on description was formerly described as "Superior to No. 1 Standard Californian Brewing Barley." This description could not be a definite statement of quality as shipments must vary considerably, but the London Corn Trade Association usually assessed it as meaning a difference better than the Standard of 3d. to 6d. a quarter. The San Francisco Exchange and Merchants Association decided in 1937 to abandon this description and sell as "about No. 1 standard." A similar sample is made up for Mariout types and referred to as No. 1 Standard Mariout barley and another of choice brewing barley.

Somewhat similar grades have been made at Adelaide for Australian Chevallier barley and designated Superior to No. 1 Standard, No. 1 Standard, No. 2 Standard and No. 3 Standard.

(37) Canadian Barley Grades.

The Ontario Agricultural College selection of Manchuria known as O.A.C. 21 is grown very extensively in Canada and is popular among Canadian brewers. It yields good malt, suitable for the

* The American bushel is smaller than the Imperial in the ratio 1 : 1.032.

American type of beer and, when of good quality, can be used with success in ale brewing when barley of high nitrogen content and enzyme activity is required for blending with two-rowed types. It is the principal type barley set up by the Canada Grain Act as amended in 1929. One of the chief enactments of this measure was the setting up of three strains of barley as types for the different grades under which malting barley should be sold. Thus Canada Western barley was based on O.A.C. 21, while two-rowed barleys have to be equal in malting quality to Canadian Thorpe. In each of these groups there are three grades of varying malting quality, together with other grades considered as grinding barley. Each of the malting grades is bound to contain a specified percentage of grain of one variety or type equal for malting purposes to the named race. There must be 95% of such barley in bulks of Grades 1 and 2 and 90% in Grade 3 Extra. Lower grades than these, intended for grinding barleys, may contain mixed varieties or germinate badly, but selected bulks of Grade 3, which falls below Grade 3 Extra, are not infrequently used for malting.

There are, in addition, similar grades based on Trebi and two-rowed grades. Trebi is a six-rowed barley of Mediterranean type usually unsuitable for malting. Since the grades cover barleys of equal malting quality to the named type and may include 5 or 10% of other types, they do not necessarily segregate varieties but they are designed to assist in bulking barleys of related varieties, equal in malting value. The two-rowed grades might include Duckbill, Hannchen, Binder, Chevallier, Plumage-Archer, or any other two-rowed barley of malting quality grown in Canada. The Canada Western six-rowed grades, based on a selected Manchuria barley, may similarly include Mariout, Bay Brewing, etc., though these are more closely related to Trebi. Some of the barleys which may find their way into the various groups are so different in malting quality, that the grades are really not sufficiently precise for malting purposes and individual selection of graded bulks is essential to avoid the uneven growth inevitable with mixed barleys. The Canadian barley imported into England is usually of Grade 3, as most of the better malting barley is used for brewing in Canada. Specifications for some of the grades are summarised in Table 2.⁷

In addition to O.A.C. 21, which is the generally popular barley, Mansury is quite widely grown and Peatland, which has been more recently introduced, is suitable for some districts. They are all similar barleys of the Manchuria type. Trebi is also grown on account of its high yielding qualities, while Hannchen and Canadian Thorpe are the commonest two-rowed varieties.

TABLE 2.—CANADA WESTERN BARLEY GRADES, 1929

Grade	Wt. per bushel lb.	Variety	Standard of quality	Limit of impurities %
No. 2 C.W.	49	95% O.A.C. 21 or equivalent malting variety (i.e., Manchurian varieties)	Sound	1
No. 3 Extra C.W.	} 48	90% of the same	Sound	1½
No. 3 C.W.		Any variety or mixture	Weather-stained, immature, shrunken, slightly frosted or otherwise damaged but sweet	6

(38) Other Six-rowed Barleys.

Among six-rowed barleys imported from other countries, the Australian Cape most nearly approaches the Californian narrow-eared type and is often of very good quality. The Chilean Brewing are bold sunny barleys of rather coarser texture well liked by many brewers.

Most of the six-rowed barleys used in England previous to the introduction of Californian came from the Mediterranean basin. Of these the Yerli Smyrna, grown in Asia Minor, was probably the most liked and is still preferred by many to any other six-rowed barley when available in good quality, which is now comparatively rarely the case. Spain also produces very good six-rowed barley, but little is seen on the English market. A very thin barley, giving a low extract, grown in Palestine and imported from Gaza, is often of bright appearance and is used to a considerable extent. Most of the Mediterranean barleys are thinner and are more husky than the Californian and are frequently delivered with a rather high percentage of dirt, which must be screened out with thin corns previous to malting. Sales are usually made on a basis of 4% dirt. A fair amount of barley also sometimes comes from Cyprus, but this is generally rather long and poorly filled.

The quantity of brewing barley obtained from North Africa, Morocco, Egypt, Algeria, Tunis, and Tripoli is much less than formerly. The best is shipped from Gabes, while Bahari barley from the alluvial lands of the Nile basin is also useful but sometimes contains a percentage of seeds of fenugreek, which must be removed by means of a half-corn separator. Other Egyptian barleys are known as Egyptian Mariout. These, though thin, are quite useful. Machiné is a name given to barley produced by

French colonists in Algeria, Tunisia and Morocco, on account of the use of agricultural machinery, which is not employed in the more primitive native cultivation. It always contains skinned corns which the native threshed grain does not. Though the extract given by these Mediterranean barleys is generally lower than that of Californians, they make sound brewing material when good shipments are available. An approximate comparison of their extracts, referred to moisture-free malt, is given in Table 3. Their 1,000-corn weights on dry barley are about 24–30 grams, and their bushel weights between 40 and 50 lb.

TABLE 3.—EXTRACT OF MALTS FROM SIX-ROWED BARLEYS

	lb. per quarter on dry malt. Ground, Seck 0.5	Per cent. dry basis. Fine grind
Californian, Atlas type	92–97	73–77
„ Coast type	89–95	71–76
„ Mariout	92–97	73–77
Manchuria and Oderbrucker	84–92	67–74
Australian Cape	90–94	72–75
Chilean	90–94	72–75
Smyrna	89–96	71–77
Algerian, Tunisian, Egyptian	89–92	71–74
Tripoli, Morocco	87–91	70–74
Gaza, Cyprus	84–91	67–73

Some of the Indian barleys grown in the Punjab, North-West Provinces and Bihar are good, but shipments have been defective and there has been much contamination with Khapra beetle. If the efforts to improve the cultivation and shipment of barley now being made by various Indian Provincial Governments are successful, there should be a considerable future for Indian six-rowed malting barleys, but until freedom from Khapra can be assured their importation is very dangerous, since it is practically impossible to eradicate this pest from buildings in which it has gained a lodgment. The barleys are generally of the *H. Vulgare* type, some having a distinctly brown or purple colour.

(39) Types of Barley and Brewing Requirements.

Most brewers have definite views, based on long experience, of the type of barley best suited to their special requirements. Not so many years ago the Goldthorpe type of barley was rejected in Burton-on-Trent, where Chevalliers had the preference for pale ales. With the introduction of Plumage-Archer and Spratt-Archer, this discrimination between wide- and narrow-eared barleys

has in large measure disappeared, but the majority of brewers prefer definite types characteristic of one or other of the barley growing districts. In some areas the system of brewing appears to have been developed to suit the local barleys, though it has been modified in many cases with increasing transport facilities to adapt it to the use of superior or different types from other districts or countries. Local adaptations of this kind still persist, for example in the north of England, where the heavier barleys seem to be more suitable for the stone square system of fermentation.

The uncertainty of the English climate with liability to immaturity in the grain, to weather damage or a possible lack of soundness in extreme circumstances has led to the very general practice of including a proportion of malt from selected foreign barley. For this purpose six-rowed barleys grown in drier countries have proved particularly useful as have the two-rowed barleys of Czecho-Slovakia. The latter are similar in composition to English barleys, and, when perfectly mature, are found by some brewers to help in regard to yeast production. The six-rowed malts yield 5 to 10% less extract than good English malt, but their husk assists in mash tun drainage and does not communicate any objectionable flavour when mashed by infusion methods. It is sometimes claimed that the more actinic light of the southern countries has some physiological effect on the barleys, and that their utility in brewing is influenced by this as well as by the difference in composition, but no definite evidence in support of this appears to be available. It might seem that the short ripening period in hot, dry countries would be likely to produce immaturely ripened grain, and it is a question whether this is not a characteristic of some imported barley, a somewhat contradictory position having regard to the favour in which most of this grain is usually held.

The European lager brewer prefers the Hanna type of two-rowed barley on account of its high extract and delicacy of husk, and, in the majority of cases, does not use six-rowed malts, because the decoction mash may extract flavouring substances from the husk. In America the Manchuria barley, with its high nitrogen content and enzymic activity, has proved particularly suitable for use with maize or rice grits, and the brewing process has been adapted to suit these materials. The rapid American malting process, usually with Saladin or other compartment systems, with germinative periods from five to seven days, and temperatures rising to between 70° and 75° F., is also suited to these barleys, but not without considerable modification to grain of the Californian or two-rowed types. The Manchuria barleys have not

generally been received with favour for brewing in England, though their suitability for producing stable, pasteurised bottled beers and the facility with which they yield a high percentage of soluble nitrogen should make them useful in blends for some purposes. The most commonly imported grain of this type is Canada Western No. 3, which is not considered in Canada to represent a malting grade of this barley. It is largely employed for malt extract on account of its high enzymic activity and selected parcels are used in very restricted quantity for brewing. It is, however, generally condemned by English brewers on account of its unattractive appearance and liability to poor germination.

(40) Summary.

Malting barleys may be divided in three very distinct types. The two-rowed barleys, mainly of Europe; six-rowed barleys of Manchuria type, typical American brewing barleys; and the six-rowed barleys of Mediterranean type of the Mediterranean basin, California, Chile and Australia. There are many variations in type in each of these groups, but they mark out the types of barley used for three distinctive brewing processes and types of beer. The lager brewers of the European Continent confine themselves almost entirely to the two-rowed European barleys. The top fermentation brewers of Great Britain and Ireland prefer a blend of the home-grown two-rowed barleys with six-rowed barleys of the Mediterranean type imported from drier countries. The six-rowed Manchuria barleys are the most suitable for American methods and beers.

The various brewing processes have to a considerable extent been developed to make the best use of the barleys grown in the countries in which they are used. The type of beer produced in any country thus depends largely on the characteristics of the home-grown barley. The climate of this country has made almost obligatory the importation of foreign barley for blending with the home-grown grain, for which purpose the barleys from the Mediterranean basin and barleys of somewhat similar type from California, Australia and elsewhere have proved the most suitable.

During the last thirty or forty years a great deal has been done to improve the yield and at the same time the malting and brewing quality of barley by selection and hybridisation. Plumage-Archer and Spratt-Archer are outstanding instances of barleys which have proved of advantage to farmers and yield better quality grain for brewing than the kinds previously grown. Similar striking advances have been made on the Continent of

Europe and in America, O.A.C. 21 of the Ontario Agricultural College being the standard barley of Canada.

It is important that brewers, particularly in England, should make themselves familiar not only with the barleys of their own country, which must remain their main source of supply, but also with the characteristics of foreign barleys. The barleys, even from different parts of England, vary in their brewing properties more on account of local conditions of growth than of variety, and these differences become particularly marked in barleys from distant countries. Since the inhabitants of any district have become accustomed to the beer of the district and the character of this beer depends on the barley which is used there and the brewing methods dictated by the malt, there is a natural prejudice against any other type. Instances of this can be found in breweries which will only use barley from one district in England, and in the tardiness with which any other type would be tried, even though it appears to be of better quality. This particularly applies to a foreign barley, as it did years ago to Californian in this country, and still does to the same barley in America, where the malting and brewing methods appropriate for the Manchuria barley do not suit that of the West Coast. The first step in brewing is to become familiar with the characteristics of all available barleys and learn to select those most appropriate to the type of beer required.

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CHAPTER IV

PHYSIOLOGICAL CHARACTERS OF BARLEY

BARLEY QUALITY

(41) Malting Quality.

The malting quality of barley is usually judged by appearance and simple physical tests. Successful as these methods generally prove in practice, they are not really adequate to determine beyond doubt its suitability for the particular type of malt and beer required, but they must always play an essential part in barley buying. Ripeness, condition or moisture content, soundness, development, texture of skin, regularity in size, shape, and colour, appearance of the cut endosperm, purity of race, freedom from other seeds and from damage caused by weather, heat, threshing, insects, fungi, etc., are among the factors taken into account. These must all be judged by hand examination, the essential qualities for malting being maturity, vitality, regularity, fineness of skin and freedom from damage. Of these maturity and regularity must be particularly emphasized. Good malt cannot be made from immature barley or from grain that has prematurely dried off in the ear and a proportion of such grain in a bulk ruins the brewing value of the malt made from it.

(42) Ripeness and Maturity.

During the development of barley there is a constant flow of carbohydrate and nitrogenous substances into the grain to be utilised in the synthesis of tissues and reserve materials. This slows down as the grain matures and its composition settles into equilibrium as the moisture supply fails. Ripening may thus be regarded as marking the completion of a long cycle of physiological changes, leading up to a point at which the living elements of the seed, under suitable conditions of desiccation, are able to pass into a dormant state and become ready for harvest. An ideal state of affairs would be marked by arrival of the embryo at the resting stage at the same time as complete development of the endosperm cells, so that the carbohydrate and nitrogenous contents of the latter would be in the most suitable condition for absorption by the young plant and in the most advantageous

relative proportions. The attainment of this condition by barley is a predominant factor in its malting and brewing quality, but unfortunately the adjustment is rarely quite accurate. Complete physiological maturation of the endosperm may not be of great importance to the plant itself, though it assumes an entirely different aspect when regarded from the standpoint of the maltster who has to produce changes in the endosperm contents in a uniform manner during a brief period of germination under artificial conditions. It was in these terms that Brown¹ described the course of maturation, pointing out that it was a matter of practical importance to find some definite criteria for determining whether barley has been physiologically matured in all its parts before its properties are finally stereotyped by desiccation.

Munro and Beaven² regarded mellowing as a change in the matrix in which the starch granules are embedded, which would be assisted by slight absorption of moisture after ripening, but no full solution has yet been found to this problem, and the barley buyer's judgment of maturity is still mainly based on the appearance and cut of the grain. Escombe's test for maturity, based on microscopical examination of the nuclei of the endosperm cells, is too tedious and delicate for general practical application, though of considerable scientific interest. As the stage of maturity indicated by mellowness is reached, the nuclei are found to have suffered great structural change and they become disintegrated by the time the cells are fully matured. From this time the starch-bearing cells are no longer able to initiate vital changes within themselves.

Definitely immature barley, harvested too early, or grain that has prematurely ripened or "dried off" can generally be detected by its pinched and unfinished appearance. A bulk should be rejected if it contains a proportion of such grain which will not modify equally with the rest when malted and is thus liable to give trouble in the brewery. In other cases considerable experience is required to decide whether the colour usually associated with maturity may not be a stain, covering up defects. The appearance of the grain may be greatly affected by rain or showers in June and early July. The stained but very mellow, well-filled barley resulting under such circumstances after the physiological processes leading to maturity have gone on regularly and uninterruptedly makes excellent brewing material, but a similar colour may hide defects due to immaturity or "dying off" after continued dry, hot weather earlier in the season. This arrests the growth at a most critical period and may give the whole bulk a poor appearance or only affect late tillers. Absence of rain or showers later in the season, after normal growth and maturation,

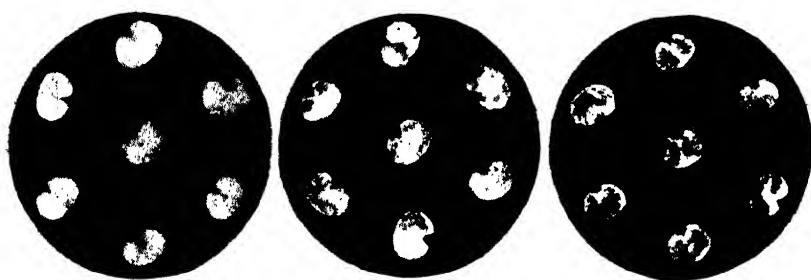


FIG. 22

CUT ENDOSPERMS OF MEALY, PARTLY STEELY AND STEELY BARLEYS

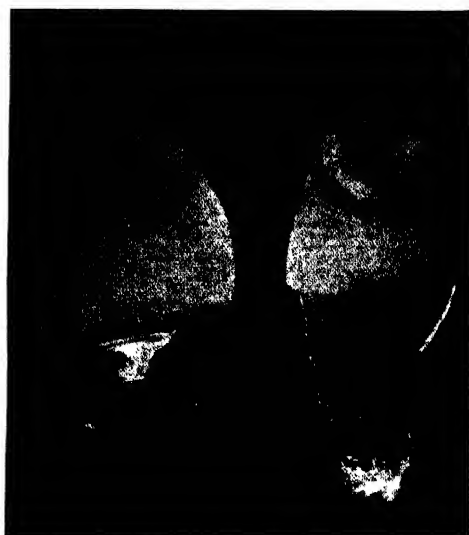


FIG. 23

DE-HUSKED KERNELS OF GOOD AND BAD MALTING BARLEYS

Facing page 55

may give white, well-formed barley with a somewhat steely cut. Such barley improves immensely by stacking or should malt well if given two or three months' rest after kiln-drying. It is usually the case that the stained barley harvested after a generally rather wet and cool season is better malting material than the white, and often more attractive grain obtained after a dry and hot summer. It is more easily modified and the malt much to be preferred for its brewing quality. The practice of drying barley at the farm, immediately after cutting, may improve its appearance, but lack of skill in this rather delicate operation may easily result in defective germination. Moistening followed by drying may also improve the appearance of barley, but this improvement is liable to be fictitious and barley suspected of this treatment should be regarded with suspicion.

(43) Mealy and Steely Barley.

The appearance of the endosperm when cut evenly across, as shown in Fig. 22, is a valuable indication of the maturity of barley. All the sections should be white, in which case the barley is referred to as mealy and may be relied on to malt readily and evenly, unless the embryo is damaged in any way. If the cut endosperms appear vitreous the corns are said to be steely. This is generally a sign of premature ripening or an indication that the barley has dried off before it has come to maturity. In some cases the individual corns show a cut that is partly mealy and partly vitreous, and the barley is judged by the proportions of mealy, steely and partly steely corns in the sample. Many samples of malting barley contain a proportion of steely corns and an idea can usually be obtained from the cut of the regularity with which they will germinate. In some cases, however, a more or less steely sample germinates quite well, so that a poor cut is not so definite a sign of inferiority as mealiness is of good malting quality. In some cases a great improvement in the appearance can be brought about by steeping followed by slow drying at a moderate temperature. This is, however, a very dangerous expedient in practice, since it is impossible to prevent incipient germination in some of the corns, with subsequent loss of germinating power during even short storage.

Mealiness is generally attributed to air spaces throughout the endosperm. It has been suggested that steeliness is due to drying down of intermediate products in the formation of starch when growth is interrupted by any cause during development of the grain. These intermediate products form a large proportion of the solids during the early stages of development, so that early arrest of growth by disease, drought or hot weather in humid

climates may lead to their conversion to steely products around the still comparatively small starch granules.

The degree of mellowness or mealiness of a barley was expressed by Brown¹ as "coefficient of mealiness." In order to determine this 500 corns are cut across in a cutter and divided into (1) mealy, (2) half mealy, and (3) steely, the percentage in each class being noted. The number 100 is taken to denote complete mealiness, one complete steeliness, and 50 the intermediate class. The sum of the percentages of each class multiplied by the appropriate figure and divided by 100 is taken as the "coefficient of mealiness." Thus a barley with 40% of mealy corns, 30% of half mealy and 30% of steely corns would have a coefficient of mealiness represented by:

$$\frac{(40 \times 100) + (30 \times 50) + (30 \times 1)}{100} = 55.3$$

The percentage mealiness can be obtained from the appearance of the endosperms shown by a longitudinal corn-cutter by dividing the number of half-steely corns by two, that of the steely tipped corns by four and subtracting the sum of the figures obtained, with the number of steely corns, from 100.

Munro and Beaven found that the total nitrogen content of steely corns is greater than that of mealy in the same homogeneous sample and that the steely corns contain a relatively high proportion of nitrogenous substances soluble in (a) 5% salt solution, and (b) alcohol of sp. gr. 0.90. Bishop's more recent investigations show that the steeliness is not due to excessive quantity of any particular protein, the various proteins existing in the same relative proportions as they do in mealy grain of the same variety and total nitrogen content. Probably the most important factor in producing the stresses and strains to which mealiness is due is the shrinking of the starch granules as their water content falls from 40% to 15%, but actual spaces in the cell contents can only form when the tensile strength of the protoplasmic matrix has been overcome. From this it might be expected that cells containing a greater quantity of protein would resist the strains better and remain steely.

(44) Texture of the Husk.

Attention is naturally focussed on the texture of the husk when judging barley from its appearance. The terms thick-skinned and thin-skinned may have little actual relation with the thickness of the husk as measurements have shown that there is practically no difference in the thickness of the husks of coarser and finer

corns selected from a homogeneous bulk. Nevertheless there is justification for this judgment of quality by external evidence. The husk belongs to the leaf system of the plant and is not part of the seed itself, but excessive manuring and other conditions which tend to produce luxuriant growth give, at the same time, coarse skin and large, high nitrogen corns, lacking in mellowness. The testa, pericarp and husks are formed before the starch-containing cells of the endosperm, which develop from the centre outwards and exert great pressure on the envelope. The skins and husks consequently become stretched and smooth when the growth of the kernel is excessive but wrinkle on to the surface of the latter when the growth is less luxuriant and typical of mealy grain.

(45) Colour of Barleys.

Many barleys are tinged with black, brown, red, purple or blue pigments. The red, purple and blue colours are due to anthocyanins, the two former occurring in the husks, the last in the aleurone layer. The existence of such minute quantities of colouring matter would hardly be expected to have any influence on the quality of the grain, but Beaven found some difference in black and white corns separated from two-rowed Ouchak barley. The white-skinned grain malted rather more freely and modified somewhat better than the greenish- or black-husked barley from the same bulk. It also showed a slightly lower diastatic activity, while the specific gravity of the black malt was greater than that of the white, but less than that of the green-skinned. The blue colour is that most frequently met with on the English market, as it occurs in many Californian barleys, to which it often gives a greenish tinge through the husks. The pigment can have no influence itself on the brewing quality of the grain as the aleurone layer in which it occurs is not converted in the mash tun but remains in the grains. Nevertheless the reception of the white Atlas strains was prejudiced at first by its absence, as it was found so generally in the older races of Californian barley and known to be associated with good brewing quality. In parts of America an opposite prejudice exists as a blue tint is often considered an index of steeliness, despite the fact that elsewhere the blue-tinged O.A.C. 21 and other Manchuria barleys are accepted as of excellent quality. It was this blue pigment, which acts similarly to litmus as an indicator for acids, that led to A. J. Brown's discovery of the semi-permeable layer in the skins of the seed, which would permit the passage of water but not of dilute acids.

(46) Shape, Size and Structure of the Grain.

Photographs of typical barleys from which the integuments have been removed are reproduced in Fig. 23. These represent a good and bad malting barley and from them it is possible to follow Mann and Harlan's² conclusions on the relation between malting quality and the morphology and physiology of the grain. If the great mass of the starch be near the embryo, as in the short, plump grain, the disintegration of the endosperm is readily and uniformly accomplished, but if it be distant, as in the long, spindly grain, complete modification of the endosperm cannot be accomplished without great malting loss. If the secreting surface be large in proportion to the size of the corn, enzymic action should be ample. It will be observed that the Standwell barley on the left has a relatively large scutellum, projecting over the flanks of the grain, which is typical of good malting barley. The area of the secreting epithelial layer is great relative to the size of the corn and the enzymes are able to diffuse readily through the endosperm before an excessive quantity of starch in the area adjacent to it is attacked and absorbed. The badly malting Finnish barley on the right is spindle-shaped with a small insufficient scutellum. These observations afford a satisfactory explanation of the maltsters' and brewers' preference for moderate-sized, plump grain.

Size affects the quantity of extract, a bold, well-matured barley being ideal in that respect, but small, mellow barley of plump shape is much to be preferred to a large, coarse barley, lacking in ripeness. On the other hand some rather small, pinched barleys would be chosen when diastatic activity is a desideratum, high nitrogen content being a good guide for that purpose. Unduly small, pinched grain, having regard to the variety of the barley, is, however, generally a sign of immaturity or premature ripening. This leads to badly modified malt and, therefore, also to low extracts and other defects consequent on the forcing to which they may have to be subjected during malting. In the British climate, two-rowed barleys are generally better both in respect of size and maturation than six-rowed barleys, but elsewhere six-rowed varieties may mature better and give finer quality grain, though often smaller in size than two-rowed grown at the same place. As between the wide-eared and narrow-eared varieties, the former are generally the larger when grown under parallel conditions, but there may be nothing to choose in quality. Beaven points out that, in comparing two- and six-rowed barleys, it must be recalled that conditions of soil and climate are the overwhelmingly determining factors in quality. From the botanical

point of view there is no specific difference between barleys of such widely different malting quality as, for instance, those grown in South Russia and in the Yerli district of Smyrna or between Brewing Californian and Scottish Bere. There may be much less difference as malting material between two-rowed and six-rowed barleys grown in the same climate than between either sub-species grown in widely different climates.

(47) Regularity in Barley.

A bulk of barley lacking in homogeneity in any of the characters previously referred to, be it variety, maturity, vitality or size, is definitely defective as a malting barley. The importance of regularity in barley is equally as great to the brewer as the maltster. Without it the latter cannot produce evenly grown malt and without evenly modified malt the brewer cannot be assured of his product.

A primary factor in the regularity of a bulk of barley or in the even growth of malt is purity of race. The morphological differences and growth characteristics on which barley classifications are based can generally be more easily applied in the field to maintaining homogeneity than in the bulking of threshed grain. Two-rowed and six-rowed barleys can readily be distinguished when threshed but the distinctions based on width of ear or density are not so definite and the increasing number of hybrid strains is constantly making it more difficult to use morphological characters as a means of differentiation, even when the barley is in ear, and the identification of threshed grain is in many cases impossible. So many selections have been made on economic and cultural grounds to increase yield, stiffness of straw, resistance to disease, to produce earlier ripening, eliminate shattering and decrease nitrogen content that the differences between the strains are only exhibited by physiological characters and are not evident in the appearance of the grain, though they may result in unevenly grown malt if barley of different races is bulked. Maltsters and brewers agree that the increasing purity of seed used by farmers has been of great help in improving the regularity and quality of malt and in many instances have co-operated in the development of improved, pure barley strains, as in the instance of Guinness with Spratt-Archer, or have interested themselves in the distribution of pure seed adapted to their particular district.

Among the most serious defects in regularity are those due to climatic conditions. These may occur through irregular growth and ripening, and ruin the malting value of barley however homogeneous in variety it may be. In some cases it may be

possible to screen out small immature corns from late tillerings without serious loss, but in other cases the percentage may be so high as materially to increase the cost of the usable grain. When the growing period in a damp climate like England has been unusually dry and hot a certain and often large proportion of prematurely ripened corns may make a bulk almost valueless for malting. At other times, through uneven growth or because the field has been cut too soon in fear of bad weather, unripe corns may be mixed with properly matured barley, when the bulk will prove equally unsatisfactory malting material. Irregularity in these respects may easily be much worse in its effects on malting quality than lack of purity of race. It is one of the first things to be looked for when selecting barley for brewing purposes and all barley showing any marked irregularity should be rejected.

(48) Damaged Barley.

Many forms of damage are encountered including those caused by weather, fungi, insects, and too close threshing which ruins many fine-skinned samples, but "Mow-burn" or "Heat" is the most serious. It may arise either because the barley was cut before it was fully ripe and was stacked before the straw or accompanying clover had had time to dry in the field or on account of wet weather during harvest. The chief danger of "heat" arises not from the corns which are actually killed and readily detected by discoloration or destruction of the embryos, but from the probability that the vitality of the barley throughout the bulk will be crippled. A superficial weather stain may have little or no effect on brewing value, though it may have reduced the barley to a lower grade on account of uncertainty as to the extent of the damage that may have accompanied it. Excessive rain around harvest time may cause the metabolic processes to proceed too far, while mould development, bacterial decomposition or growth may occur in barleys left in the field or stored with a high moisture content. The damage caused in either event can readily be detected and seriously detracts from the malting and brewing quality of the barley. Heating is a sign of destruction comparable with internal combustion. Loss of germinative activity is a proof of the commencement of decomposition. The number of dead corns may in themselves cause serious trouble, but it is slight in comparison with the damage due to putrefactive changes brought about by bacterial agency, which may possibly lead to instability in the beer.

(49) Germination.

Almost every corn of a good malting barley should be capable

of germination and, what is of equal importance, they should all germinate at the same rate. Germination tests are consequently very frequently carried out, the results being given in terms of "germinative energy" and "germinative capacity." The former is measured by the percentage of corns which chit in 72 hours when submitted to growth tests on moist blotting paper or on sand in a germinating apparatus at a temperature of about 65° Fahr. Under these conditions not less than 97% of the corns should show signs of growth in 72 hours. Germinative capacity represents the percentage of corns which germinate when the test is continued for a longer period. It should not be less than 98% and in good malting barleys is usually almost or quite complete. English barley will very often not germinate satisfactorily until it has been kept in the stack for a considerable time or unless it is kiln-dried.

In England a period of two or three months is usually allowed between harvest and commencement of malting, to ensure even growth. Chemical and physical changes in the grain are almost stopped by the desiccation which accompanies ripening, but the subsequent improvement in germinative activity during the resting period shows that the apparent cessation of vital processes was not complete. Post-harvest maturation, whether under the drying influence of air currents in the stook and stack or assisted by kiln-drying and the subsequent rest, has a most important influence on the malting quality of barley. To what extent the maturation depends on drying or is assisted by the heat which accompanies it and what chemical or physical changes occur in the grain are by no means definitely known.

(50) Barley Drying.

Since English barleys so frequently contain between 16% and 20% moisture when harvested, it is generally desirable to kiln-dry them immediately after purchase and reduce the moisture content to between 10% and 12%. The practical result is that the danger of heating and mould growth during storage is reduced or eliminated and germination becomes even. Drying is carried out either on a kiln or in a drum at a temperature not exceeding 125° Fahr., or, preferably, at about 110° when sufficient air draught is available to reduce the moisture to the desired extent in 12 hours. Germination is frequently practically perfect immediately the barley comes off the kiln, but after 10 or 14 days it may lose its germinative power to the extent of 40%, after which it gradually regains it until the best germinative results are obtained after about six weeks' rest.

The Combine harvester is becoming increasingly used on large

farms, where the barley is dried immediately after threshing. By this means a sample of finer appearance and greater market value should be obtained. There is a danger, however, that the vitality of the barley may be affected by lack of skill in the delicate process of drying and by use of unduly high temperatures. For this reason farm-dried barleys have been prejudiced on the market, and arrangements were made that all such barleys should be marked as dried to protect the buyer. There can be no doubt that use of the Combine harvester will increase, and, with greater experience in its use, this should be to the advantage of the farmer, and no detriment to the purchaser. The malting value of the barley should indeed be increased.

(51) Blending of Barley.

Skilful grading of barley for bulking preparatory to malting is of vital importance to the brewer, who will ultimately use the malt made from the bulks. Though it is customary to blend several types of malt in a brewery grist, it is essential that each of them should be evenly malted, and this cannot be the case unless the individual growths in the bulk were homogeneous and well matched one with another. The difficulty of identifying and separating parcels of threshed grain of different varieties makes it necessary to look for the varying response to the conditions of growth which mark them out in the field. Even in closely allied strains some ripen earlier than others. In addition it is not good practice to bulk evenly ripe growths of different strains because they may not germinate at the same rate, giving a proportion of undermodified malt in the bulk, much to the distress of the brewer obliged to use it. Spratt-Archer, for instance, generally malts more quickly than Plumage-Archer. The growth characteristics of wide- and narrow-eared barleys are different on the floor as well as in the field. Variations in type and quality naturally occur in all districts, even with the same seed, and occasionally it may be possible to bulk barleys grown in widely-separated counties with greater success than other growths from neighbouring fields. It is, for example, frequently possible to match barleys grown on sheep-folded land on the Wiltshire Downs with grain from Norfolk.

Seasonal effects may be very marked and differ according to the nature of the soil. In some years there is a mixture of small immature grain from late tillerings or a proportion of flat-backed steely corns which ruins the homogeneity of the growth. Very dry seasons may be fatal to maturity on light lands, the barley drying off in the field before it is ripe. A portion of such grain in a bulk of barley may be the source of endless trouble in brewing.

Many grades are thus required to cover the variations produced by variety, soil and season. The essential points considered in grading include :

(1) Type or variety, which generally resolves itself into differentiation between wide- and narrow-eared barleys, followed by separation into races of each when possible.

(2) Soil—the barley in each grade must be grown on similar soil.

(3) Quality—expressed by kindliness or freedom in working.

(4) Regularity in size with approximately the same bushel weight.

(5) Conditions of harvesting—e.g., weathered and unweathered barleys should not be mixed as they would not grow evenly, even if similar in other respects.

The bulks should thus contain only barleys of the same strain, equal nitrogen content and even germination. They will prove less regular in malting and less satisfactory in brewing the further they depart from this ideal. In practice bulks will frequently contain growths of different but allied strains. If these have been carefully matched, the result is usually less detrimental to even malting quality than bulking of the same race in varying states of maturity. The ideal course is, however, to keep every growth separate for malting as it is to keep every kiln of malt separate for brewing, an ideal which often cannot be attained. The variations in individual growths make the large malt silos, which are so convenient for large bulks of even malt, much less suitable in this country than elsewhere.

FUNGOID DISEASES AND INSECT PESTS

(52) Fungoid Diseases.

Such parasitic fungoid diseases as Smut and Rust, which do great damage in the fields, should not make themselves apparent in the brewery as barley known to be infected is not malted, but occasionally traces of their effects may be detected in malt. Two types of Smut are differentiated as “covered smut,” *Ustilago hordei*, and “naked smut,” *U. nuda*. The former replaces the grain in the ear with a thinly covered, blackish mass of spores each of which measures 6–7.5 μ in diameter. The spores of naked smut are somewhat similar but rather browner and occur loosely on the diseased ears, which they destroy until only the rachis is left. Covered smut is commoner in the northern barley districts of Yorkshire and Scotland than in the south where naked smut is more commonly found.

Among other fungoid diseases causing widespread damage are the Black, Brown and Yellow Rusts, *Puccinea graminis*, *P. simplex* and *P. glumarum*, which attack the sheaths, stalks and leaves of barley, Leaf Stripe and Spot disease, *Helminthosporium graminum* and *H. teres*, which attack the leaves, while their mycelia extend into the growing part of the shoot causing blindness or killing the plant, and *Ophiobolus* or "take all," a destructive fungus causing root rot. It has been suggested that many barley corns described as weathered have been attacked by *H. teres*. These fungi do not develop on the malting floor.

A mildew, *Erysiphe graminis*, and Black Blight, *Cladosporium herbarum*, occur on decaying corns as a dark coloured mass of conidiophores bearing orange-coloured, elongated septate conidia $18-20 \times 8-10 \mu$. According to Mason they give rise to secondary spores, which when grown on wort agar resemble wild yeasts. They attack the embryo and reduce the germinative power of barley. An Ascomycete, *Giberella Saubinetti*, which attacks the plant both above and below the ground, ultimately killing it, has been a source of serious trouble in some parts of America, as infected grain fed to hogs causes vomiting. This "scab disease" and *Helminthosporium* are principally responsible for "blighted barley" in America, but they cannot be easily distinguished in threshed grain in which many forms of blight cause a similar appearance.

The Red Mould, *Fusarium hordei*, familiar on malting floors, is possibly the conidial stage of *Giberella*. The conidia are crescent shaped and septate, $35-45 \mu \times 5-5.5 \mu$ to $60-75 \mu \times 4-5 \mu$. They form an ochreous mass on infected malt. Signs of this and other moulds which may have developed on the malting floor are sometimes seen on damaged corns in malt, but the extent of the infection should be insufficient to cause any damage to flavour in the beer. (Mason.⁴)

(53) Insect Pests.

The larvæ or grubs of a number of beetles and flies make serious depredations on growing barley by attacking the plants below ground. The commonest are the long, yellowish, hard-skinned grubs of several species of Click beetles which are generally known as wire worms. In addition the "white grub" or larva of the cockchafer and the "leather jacket" or larva of the daddy-long-legs may attack the roots so seriously as to destroy the corn in patches over a field. The larvæ of the gout fly and frit fly and the eelworm attack the growing shoots and may also do a great deal of damage. (Mason.⁵)

It is, however, the insects which destroy stored barley that

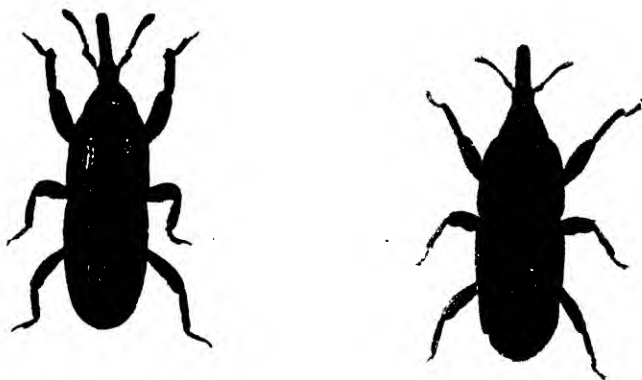


FIG. 24
GRAIN WEEVILS, *CALANDRA GRANARIA* AND *CALANDRA ORYZAE*

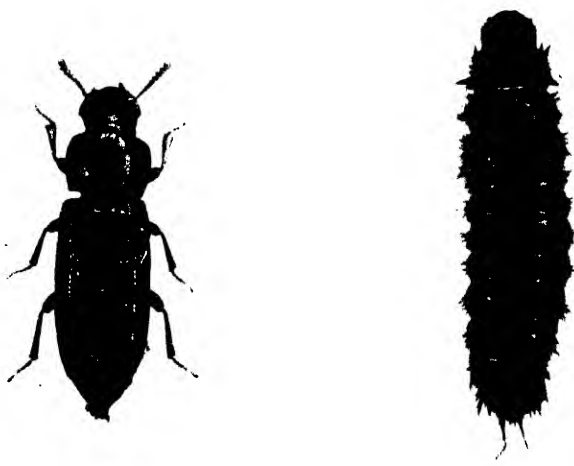


FIG. 25
KHAPRA BEETLE AND GRUB ($\times 10$)

make their depredations most clearly known to brewers and occasionally give rise to serious loss. The commonest of these are the grain weevils, *Calandra granaria* and *Calandra oryzae*, which can readily be recognised by their dark brown colour and prominent proboscis. Both these beetles are about one-tenth inch long and very similar in appearance, but can be differentiated by red markings on the back of the latter. Photographs of both species are given in Fig. 24. A little round hole in the corn is made by the proboscis of the female and in it she lays her eggs. These may number 576, laid over a period of 149 days, and, as they hatch out in three to five days, multiplication may be very rapid under favourable conditions, their development in barley occasionally raising the temperature quite considerably.

The Khapra beetle, *Trogoderma khapra* or *T. granarium*, of which an enlarged photograph is given in Fig. 25, is an even more dangerous pest than the weevil on account of the great difficulty encountered in its eradication. It occurs commonly in Indian barleys, leading to serious restriction in the importation of barley from India. Probably several related insects are included under the name of khapra beetle, the species not yet being properly differentiated. The mature beetle is about one-tenth inch in length, the male being of a darker colour than the rather larger female. The eggs are laid in the furrow or elsewhere on the surface of the grain and the damage is done by the larvæ, which are yellowish-white grubs covered with reddish-brown hairs. These are rubbed off rather easily, but the grub becomes firmly attached by them to any sacks in which it may occur.

Eradication of weevils and khapra, particularly the latter, is so difficult that the greatest care should be taken to prevent delivery of barley in which either the insect itself or punctured corns are visible. Special precautions are essential to prevent their access to barley stores. Foreign barleys should be closely inspected, Indian particularly for the khapra beetle. Floors and walls must be kept as free as possible from crevices and cracks. Accumulations of sweepings must not be permitted, while infested sacks may prove a ready source of danger. Total elimination by fumigation appears to be impossible. Chlorine has been tried with some success, liquid chlorine being used as the source of the gas, while walls, etc., are treated with hypochlorite solutions containing 15% of chlorine but chloropicrin is probably the most effective fumigant.

Great care must be taken to avoid the introduction of weevils or khapra, particularly the latter, into malt bins or lofts by infected sacks or otherwise. Khapra larvæ become active in malt at 75°–80° Fahr., and precautions must be taken to prevent rise of

temperature in the malt through direct sun rays, kiln fires or steam pipes. Should multiplication occur, the temperature and moisture content of the malt will rise. Crevices in the walls become infested with larvæ which cannot be destroyed by the fumes from burning sulphur. The following mixture used freely and applied as a spray or by brushing to the walls of the empty loft has been found to be effective by Baker and Ward⁶: Methylated spirits, 30 volumes; Ammonia solution 0.880, 10 volumes, with 60 volumes water.

(54) Summary.

The essential qualities in malting barley are vitality, maturity and regularity. Without these it cannot malt evenly and serious defects are liable to give rise to trouble in brewing. Experienced judges can detect defects in these qualities and in the condition, purity of race and freedom from damage of the sample by hand examination, a faculty which all brewers should endeavour to cultivate. A corn cutter is of great help in judging barley, showing at once the percentages of mealy and steely corns in a sample. Germination tests should also be carried out in cases of doubt. Equal care must be taken in bulking different growths as in selecting the individual samples in order to secure evenly grown malt. Reliance should not be placed on small samples in envelopes which may have dried out or been polished by handling.

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CHAPTER V

COMPOSITION AND QUALITY OF BARLEY

COMPOSITION OF BARLEY

(55) Constituents of Barley.

The constituents of barley may be regarded from the point of view of different structural elements or from that of the chemical composition of the substances existing in these. Both have their importance in respect of the brewing quality of barley and both are subject to wide variations depending on the variety and conditions of growth. Thus the husks may account for 6 or 7% of the total weight in European two-rowed barleys or twice that quantity in six-rowed varieties, while the protein content of most varieties may range from 7.5 to 15% of the dry weight of the grain, the starch content varying in the reverse direction from about 60 to 50%. The moisture content may range between 10 and 20%, according to the climate or weather at harvest time. These figures do not represent the possible limits, but cover the great majority of malting barleys and the following analyses of a two-rowed and of a husky six-rowed barley, both containing 1.6% of nitrogen on dry matter and dried down to a moisture content of 10%, must consequently be regarded as very generalised, though fairly typical of average barleys used for brewing in England.

TABLE 4.—GENERALISED ANALYSES OF BARLEYS

	Two-rowed	Husky six-rowed
	%	%
Starch	60	52
Sugars	2.5	2.5
Hemicelluloses, Pectins, etc. .. .	8	11
Cellulose	4	7
Lignin	1.5	3
Protein and other nitrogenous substances ..	9	9
Fat (ether extract, contains traces resins) ..	2.5	2.5
Ash	2.5	3
Tannin	small quantity	
Water	10	10

The starch, hemicelluloses, pectins, cellulose, lignin and proteins exist as colloidal complexes with which some of the mineral constituents are associated. It is very difficult to define them chemically and in most cases a sharp differentiation of individual substances or groups of allied substances cannot be made. This will be made clearer in the sections dealing with their chemistry and the changes they undergo during malting. In this chapter they are regarded in the simplest manner. The only analyses commonly made for the valuation of barley, apart from an estimation of the potentially available extract, are determinations of moisture and nitrogen content, the protein being calculated from the latter by means of the conventional factor 6.25. Though the loss of weight found by drying at temperatures between 212° and 220° Fahr. would appear to be a simple estimation of moisture content, there is no certainty that some of the water driven off was not chemically combined or that all the non-combined water has been removed.

(56) Barley Husks.

Barley loses about 0.5 to 1.5% of its dry weight when steeped, the greater proportion being derived from the husk. The soluble matter consists of mineral matter, nitrogenous substances, sugars, tannin, gum, colouring matters, etc., but sufficient soluble material remains to have a considerable influence on the flavour of beer. Degeneration of bottom-fermentation yeast was attributed by Moufang to toxic substances in the husks, to which the name of "testin" was given. According to Lüers, these are probably absorption complexes of tannin with proteins. Moufang advised that these should be removed from barley by steeping for a short time in warm, weakly alkaline liquor.

TABLE 5.--ANALYSES OF BARLEY HUSKS

					Per cent. on dry substance		
					5.9	—	10.8
Ash	5.9	64.9	
		SiO ₂		5.7	
		P ₂ O ₅		2.8	
		Ca		2.1	
		Mg			
Resin and fat	2.2		2.3
Protein	5.9		7.7
Cellulose (fibre)	—		24.4
Hemicelluloses (pentosan)	38.0		21.6
Other nitrogen-free substances	—		24.4
Starch	—		8.8
Tannin	—		1.0

The first analysis of barley husk in Table 5 is due to Lüers,¹ the second to Geys. The tannin content is approximated from Hartong's analysis of 12% mash tun wort in which he found 0.0111%. According to Fink, pectins, though certainly present, occur only in small quantity in barley and malt and none is represented in these analyses. It will be noted that silica is the predominant constituent of the ash of husks.

These analyses of husks may be compared with that of spent grains in Table 6 by Bishop.² This shows the quantity of insoluble or unconvertible substances present in barley. The "pentosans" partly measure the hemicelluloses, though a portion of the latter may be included in the "dilute acid extract" and another part in the "cellulose." The difficulties of analysis make it impossible to give exact figures for the various groups of carbohydrates present, or to be more precise in describing the fractions determined.

TABLE 6.—ANALYSIS OF SPENT GRAINS OF ENGLISH MALT

	Per cent. on dry substance	
	Spent grains	Calculated to malt
Ash	4.6	1.1
Ether soluble	6.4	1.5
Dilute acid extract	28.8	6.8
Lignin	17.3	4.1
Acid insoluble protein	11.8	2.8
Pentosans	9.8	2.3
Cellulose	16.7	4.0

The constituents of barley may be divided in two main groups, the carbohydrates and proteins, with smaller quantities of mineral matter and fats. The carbohydrates and proteins are distributed partly among the structural elements of the grain and partly exist in the form of reserve material laid down during growth in the cells for utilisation by the germinating embryo. The brewing value of barley comes largely from the extract or amount of soluble matter it can yield in the mash tun after malting. This is derived mainly from the reserve carbohydrates and to a much smaller extent from the proteins and structural elements. The mineral constituents are of great importance in brewing, but the greater proportion of the fat or substances soluble in ether remains in the mash tun grains. About 10% of the dry matter can be extracted from finely ground barley by means of ice-cold water. This consists mainly of mineral salts, sugars and nitrogenous substances, with the husk constituents already mentioned.

Enzymes, vitamins and bios, or the substances from which

the accessory growth factors are elaborated during germination and on which the development of yeast depends so largely, are not referred to in this chapter, but they are essential to the brewing value of barley and will be dealt with elsewhere.

(57) Starch.

Between 80 and 90% of the dry weight of barley consists of carbohydrates and allied substances. Of these starch is the most important. Existing in the form of large and small granules (Fig. 88) in the cells of the endosperm, it is the chief carbohydrate reserve material in the grain and serves as the main source of sugar for the germ during malting or germination. The available methods for determination of the quantity of starch in barley are not very satisfactory, and in brewing practice it is customary to regard the insoluble constituents which ultimately yield carbohydrate extract in the mash as "starch." The extract of barley, determined by gelatinisation and diastatic conversion, varies between 70 and 80% of its dry matter and is conventionally, but not very accurately, assumed in some laboratories to be 14.75% greater than the starch content. The extract contains soluble mineral substances, sugars, pentosans, pectins and conversion products of pentosans or hemicelluloses, as well as those of starch.

(58) Cellulose, Hemicelluloses, Pectins, Gums and Lignin.

Cellulose is the main structural constituent of the husk and constitutes some 4 to 6% of the dry weight of barley. It differs from starch in its greater resistance to water, chemical agents and enzymes, and remains unaltered during malting and brewing. Hemicellulose is the name given to a group of substances which differ from cellulose in that they are soluble in weak alkali and more readily attacked by dilute acids or enzymes. In some ways the hemicelluloses occupy an intermediate position between the reserve and structural carbohydrates, starch and cellulose respectively. They are in part hydrolysed by cytase during malting, and in part remain in the spent grains.

Many years ago O'Sullivan³ extracted lævo-rotatory carbohydrates from barley, which he called amylans. These represented about 2.8% of the dry weight of barley. C. J. Lintner subsequently isolated a similar gummy substance and Lindet another gum. So-called "amylans" representing 6 to 10% of the dry weight of the barley were also prepared in the Guinness Researches.⁴ When the ash, proteins, sugars and starch in barley are determined by the available methods, their sum always falls short of the extract obtained from barley by gelatinisation and conversion, by a quantity equivalent to that of the "amylans."

Our knowledge of these substances is very fragmentary and incomplete, but, according to H. T. Brown, the solution of the highly colloidal gum of barley is one of the most significant changes which mark its conversion into malt. They may be regarded as included in the group which is now generally referred to as hemicellulose, the quantity of "amylan" found by Brown corresponding to estimations of hemicellulose in barley.

Pectins, which show some analogy in constitution with the hemicelluloses, have been stated to exist in small quantity in the cell walls of which they were held to constitute the middle lamellæ. Nanji and Norman came to the conclusion that pectins did exist in malt but their methods of analysis were not free from criticism. In so far as these substances, the hemicelluloses, pectins and possibly other allied compounds, are soluble in water or are converted to soluble products, they may be supposed to have some influence on the palate-fulness and head-retaining properties of beer on account of their colloidal nature.

Lignin is typical of woody tissues in which it occurs as a kind of cementing material, as pectins may among softer tissues. Little is known of its composition, though it contains hydroxyl and methoxyl groups and probably an aromatic nucleus. It is soluble in strong acids but precipitated on dilution. Any present in barley may be assumed to remain in the mash tun grains.

(59) Nitrogen and Protein.

Although the nitrogen content of barley rarely exceeds 2.5% of its dry weight, the proteins in which it mainly exists have a most important influence on the properties and brewing quality of the grain. Barley also contains a small quantity of protein breakdown products, accounting for some 8 to 18% of the total nitrogen. The proteins and derived substances may amount to between 7 and 15% of the dry weight of the grain. Few barleys contain a smaller percentage of protein than 7% and few containing more than 12% would be accounted as malting barleys, unless required for purposes for which their high enzymic activity was necessary or unless they belonged to the Manchuria group which malt easily with 15% of protein or even more.

The quantity of protein and other nitrogenous substances in barley is usually assessed by determining the total nitrogen by the Kjeldahl process and multiplying this by the conventional factor 6.25 to give the percentage of protein, under the assumption that proteins contain, as an average, 16% of nitrogen (see Section 117). It is preferable to express the quantity of protein and other nitrogenous substances present in terms of the nitrogen they contain, as so much per cent. of total nitrogen, hordein-nitrogen, amino-

nitrogen, etc. Since barley may contain very variable quantities of moisture, usually between 10 and 20%, it is necessary to allow for this and express the nitrogen as a percentage of the dry weight of the barley in order to obtain comparable figures.

(60) The Proteins of Barley.

Osborne⁵ established the existence in barley of four proteins or groups of proteins, distinguished by their varying solubility. He held that three of these were clearly defined individual substances, but the chemical constitution of none of them is yet known. The protein fractions obtained were as follows :

An *albumin*, soluble in water and dilute salt solutions and in alkali, constituting 3% of the total protein. (Leucosin.)

A *globulin*, soluble in salt solutions and in alkali, 18% of the total protein. (Edestin.)

A *prolamin*, soluble in 75% alcohol and in alkali, 38% of the total protein. (Hordein.)

A *glutelin*, soluble in alkali in the absence of salts, 41% of the total protein of the sample analysed.

The names Leucosin and Edestin were applied by Osborne to the albumin and globulin in the belief that they were identical with corresponding proteins in other plants, to which these names had been given, but since the barley proteins probably differ from these it is advisable to refer to them as barley albumin and barley globulin respectively. Hordein appears to be a definite protein peculiar to barley.

Bishop⁶ developed improved methods for separating the barley proteins, based substantially on the methods used by Osborne. The finely ground barley was extracted successively in 5% potassium sulphate solution and 70% alcohol. The first extraction removed "salt-soluble proteins" including albumin and globulin with the small quantity of protein degradation products present. Alcohol then extracted the hordein or "alcohol-soluble protein," and the glutelin remained behind. The alcohol-soluble fraction obtained in the manner described by Bishop is almost certainly a definite protein, hordein. The salt-soluble fraction is, however, a mixture of substances with varying solubility. The quantity extracted may, consequently, be influenced by the physical state of the grain or by variations in analytical technique. This would correspondingly affect the percentage of glutelin, which is found by difference.

Representatives of the albumin, globulin and glutelin groups exist in almost all plant cells, but the prolamins are peculiar to cereal grains. Hordein appears to be the reserve protein of the

barley corn, serving as the embryo's chief supply of nitrogen. In this it is analogous to the reserve carbohydrate starch, from which the germinating embryo derives most of the sugar it requires. There is also an analogy in the quantity in which hordein and starch are stored in the grain. Just as a greater proportion of the carbohydrate is converted into starch when more carbohydrate is available, so a greater proportion of the proteins exists in the form of hordein when the total protein increases (Section 66). Further, just as six-rowed barleys have a smaller proportion of their total carbohydrate in the form of starch than two-rowed barleys, so they have a smaller proportion of their total protein in the form of reserve hordein than two-rowed barleys with the same protein content.

(61) Factors influencing the Nitrogen Content of Barley.

It is worth while for the brewer to study the factors influencing the nitrogen content of barley in order to be prepared each season for variations in quality and be guided to favoured districts for purchase of his requirements when the weather has varied in different parts of the country. The most important factors are soil and weather. (Russell and Bishop.) Medium and light loams are the most favourable to malting quality, sandy loams the most speculative. The nitrogen content, on the average, decreases in inverse order to yield according as the soil is sand, clay, loam or chalk. Fen-lands give both yield and high nitrogen. The effect of reasonable manuring is comparatively slight, but excess raises the nitrogen content and depresses quality. If correctly applied it can at the same time increase yield and diminish nitrogen percentage, since the carbohydrate content is raised more than proportionally.

Bad tilth and late sowing tend slightly to increase the nitrogen content but the dominant factor in England is rain in April, May and, in some districts, June, which markedly depresses it. As the plant develops it takes up nitrogen from the soil and builds it up into protein and at the same time constructs its carbohydrate material by photosynthesis from the CO_2 of the atmosphere. In the course of time simple substances of each group pass into the grain, there to be built up into structural elements or laid down as reserve carbohydrate and protein. The relative rate at which these two groups of substances are formed in the grain and, consequently, their relative quantities when the growth comes to an end depend mainly on soil and season, in particular on the period of growth at which rain is most abundant. The nitrogen content is largely determined by the percentage of nitrogen in the plant when grain formation commences in May or June, and

is little affected by summer weather, which has its chief effect on maturation and germinative activity, while harvest conditions finally determine the value as malting material. Though summer weather has little effect on the nitrogen content it has a predominant influence on the physiological condition of the grain at harvest, that is, on its malting quality. Continued drought and heat previous to maturation lead to steely barleys with irregular or defective germinative activity, such as are frequently referred to as prematurely ripened. Late tillering produces a large proportion of small, under-developed corns. Inclement weather at harvest results in unsound grain with a high moisture content.

(62) The Ash of Barley.

The quantity of mineral matter in barley varies rather widely according to the nature of the soil and other conditions of growth. It usually amounts to between 2 and 3·5% of the dry weight of the grain, when determined as ash after incineration. Two typical analyses of the ash are given in Table 7 : (A) by Moritz and Morris, and (B) by Leberle. Barleys also contain small traces of other metals such as zinc, aluminium, manganese, copper.

TABLE 7.—ASH OF BARLEY

	Per cent. of Ash	
	A. English	B. German
Phosphoric acid, P_2O_5	31·2	35·0
Potash, K_2O	14·4	21·0
Silica (as soluble silicic acid), SiO_2	23·4	} 26·0
„ (insoluble)	9·3	
Magnesia, MgO	8·3	8·0
Lime, CaO	5·0	3·0
Soda, Na_2O	4·9	2·5
Ferric oxide, Fe_2O_3	1·4	1·5
Sulphuric acid, SO_3	1·3	2·0
Chlorine, Cl	0·8	1·0
Other metals, zinc, aluminium, manganese, copper, etc.	traces	traces
	100·0	100·0

It will be noted that about half of the ash is accounted for by potassium phosphates, and that magnesia and lime also occur in considerable quantity, the magnesia predominating. The P_2O_5 content of English barleys varies little from about 1% of the dry matter of the grain (Crowther⁸). The silica is also an important constituent, existing chiefly in the husks. The

phosphates mainly occur in organic combination, but Prior found that the acidity of barley was mainly due to primary phosphates. Those present in 100 grams of dry barley required about 80 ml. of N/10 caustic soda for neutralisation, organic acids also present only requiring about half or one-third of this quantity of alkali. Calcium and magnesium phytate or phytin, the phosphoric ester of the ring sugar inositol which was shown by E. V. Eastcott to be a constituent of Bios, is believed to occur largely in the husk.

Quantities of silica varying between 0.47 and 1.83% or between 25 and 48% of the total ash were found in malt by Comrie.* It may be of importance on account of the facility with which it enters into the colloidal state in which it may produce a haze in beer. Certain characteristics of barley were found to be associated with the quantity and structure of the fragments of silica obtained from the husks. Thus when Egyptian and Hama malts were ashed they showed a number of longitudinal ribs or thickenings of narrow fibres, absent from other barleys but in accordance with their distinctive hard grinding properties. These particular malts also contained a high percentage of silica, 1.835 and 1.010% as compared with English and Californian malts, which contained 0.778 and 0.682% respectively. Their total ash content was not much greater than that of other malts, viz., 2.77 and 2.57%, as compared with 2.41 and 2.42 in the English and Californian. Comrie's observations also suggest that sufficient specific differences exist in the microscopical appearance of the silica particles to offer a means of distinguishing one barley from another.

During malting a proportion of the mineral constituents of barley are liberated from their organic combinations by enzymes. They may thus have some influence on malting quality through the form in which they occur or the manner in which they are combined with organic substances. A further quantity of mineral phosphates, mainly potassium phosphates, is liberated during mashing and reacts with the salts in the mashing liquor, as detailed in Section 885. The mineral constituents of barley thus have an important place in determining the brewing quality of barley, through their effects on the acidity of the mash, the conversion of carbohydrates and proteins, their value as yeast nutrients and by their contribution to the organoleptic properties of beer.

NITROGEN AND QUALITY

(63) Nitrogen Content and Malting Quality.

The problems faced when studying the quality of barley from

the aspect of composition in relation to the criteria applied on the market are very complicated and, to quote H. T. Brown, "the work of the physiologist must go hand in hand with that of the chemist if the problems suggested by agricultural and malting practice are ever to emerge from empiricism and acquire a rational scientific basis." Ordinary organic chemistry is baffled by a problem which is apparently more intimately related with the colloidal state of substances than with their specific nature, and there is one aspect of quality which has not yet been reduced to terms of ordinary chemical composition. It is that dependent on the nature and activities of the enzymes or agents which function during germination and govern the changes in composition during malting and brewing. Difficulties encountered in investigations of the carbohydrate constituents of barley have hindered the study of their relation to quality, except in so far as the yield of extract is concerned. The relation of the nitrogen content of barley to its malting quality is, however, a matter of direct practical observation. The superior malting quality of low nitrogen barleys, comparison being made between barleys of the same or related varieties and provenance, is so definite and the influences which determine the characteristics by which a judge picks out the best malting barleys and rejects others are so closely related with nitrogen content, that some connection between nitrogen content and quality is certain.

As an example of the concordance between market valuation and nitrogen content with barleys of the same variety grown in the same district, some figures relating to Spratt-Archer Norfolk barleys shown at a Conference at the Rothamsted Agricultural Station in the autumn of 1935 are quoted in Table 8. The barleys

TABLE 8.—RELATION BETWEEN NITROGEN CONTENT AND MARKET VALUATION
NORFOLK SPRATT-ARCHER BARLEY, 1935
(NITROGEN % ON DRY MATTER)

Grade	1	2	3	4	5	6	7
	1.28	1.31	1.28	1.30	1.46	1.72	1.52
	—	1.38	1.48	1.47	1.33	1.46	1.43
	—	1.32	1.48	1.46	1.54	1.47	1.62
	—	1.32	1.40	1.42	1.42	1.53	1.54
	—	—	1.41	1.43	1.46	1.47	—
Average	1.28	1.33	1.41	1.42	1.44	1.53	1.53

were graded before the analyses were available, and it was found that explanations were forthcoming for many of the exceptions to the general rule of higher nitrogen content, lower grade. Thus

the first sample in Grade 3 was degraded on account of irregularity, and the comparatively high nitrogen of the first in Grade 6 is typical of barley grown on sandy soil, while the first barley in Grade 4 was autumn sown. It must not be assumed that such a close correlation between nitrogen content and malting quality exists in all barleys. It is varied by varietal characteristics and cultural conditions, but it holds as a broad generalisation and is particularly marked with barleys of the same variety grown under the same conditions.

In general, lower nitrogen content, in any one variety, is reflected in better appearance, enhanced mellowness, greater ease of malting, smaller malting loss and higher extract, but lower diastatic activity. Barley of the highest class has these characteristics and, being restricted in quantity, commands a relatively high price. The nitrogen content as a rule, but not always, produces a distinct effect on the appearance of the grain, and is consciously or unconsciously taken into account by experienced judges. In some cases the malting quality does not follow the depreciation in external appearance and a more accurate assessment of malting value would have been obtained by determination of nitrogen content. The nitrogen content of barleys grown abroad is not so readily judged by buyers experienced only in the barleys of their own country. Thus, many foreign barleys have a higher nitrogen content than their appearance would suggest to a buyer accustomed to English barleys only.

The nitrogen content is, however, only one factor among many that contribute to quality and cannot be applied as a criterion to all barleys without taking others in consideration as well. Among these are variety, soil, season and maturity. The Manchuria barleys grown in the United States of America malt very readily, though they contain over 2% of nitrogen, a quantity which is generally fatal to the malting quality of the six-rowed barleys of California or the two-rowed English barleys. This comparison is between extremes, but smaller differences are shown by more closely allied races. Club Mariout does not usually malt so easily as Atlas with the same nitrogen content, and Plumage-Archer differs from Standwell. These comparisons apply to sound, mature barleys and they suggest that the differences in malting quality exhibited by varieties may depend, in so far as they are due to nitrogen, on variations in the proportions of the individual proteins. It is a short step to suggest that similar differences in barleys of the same variety are influenced by the proportions of the individual proteins. Even if this should prove to be the case, evidence will be given to show that the total nitrogen content is an equally good guide to quality.

For practical purposes the malting quality of barley is determined by (1) its variety ;

(2) its total nitrogen content ;

(3) its maturity and physiological condition.

It would be premature to say more than that the malting quality is probably influenced by the relative proportions of the individual proteins. Variations in the relative quantities of some of the carbohydrates may be equally important, while variations in the colloidal state of both proteins and carbohydrates may be much more significant than the differences revealed by chemical analysis, suggesting a return to the physiological studies which must accompany chemical investigation of the relation between barley composition and quality and emphasizing the first importance of maturity. The value of the nitrogen determination is that the analysis is simple, the result concrete and, as will be shown, related to the quantities of other constituents in a definite manner. It is therefore the most useful and practical criterion of quality, but must be interpreted in relation to variety. This important point will be developed in succeeding sections.

(64) Nitrogen Content and Brewing Quality.

Even though it be accepted that variety, maturity and nitrogen content of barley are the essential criteria of malting quality, it does not follow that the barley which malts most readily and gives malt of the best appearance at the least expense is necessarily the best for brewing. There is no doubt that an insufficiently modified malt of high nitrogen content is a bad brewing material, but it is not possible to specify, for all types of beer or methods of brewing, what degree of growth determines satisfactory modification and a high nitrogen barley is not always to be condemned. "Only six-row barleys of Manchuria type can be considered as first class for the preparation of chill-proof beers, especially pasteurised bottle beers." This is a quotation from the 1908 Edition of the Wahl-Henius *Handy-Book of Brewing and Malting*, and refers to barleys with a "normal" nitrogen content of 1.6 to 2.24%, and a thousand-corn weight of between 22 and 35 grams on dry matter. With these barleys the rule of superior malting quality with lower nitrogen content still applies, but "lower" is a relative quantity and Manchuria barleys malt readily with a higher nitrogen content than most other kinds. The expressed preference for the high nitrogen Manchuria barleys may depend to some extent on the malting methods usually adopted in America, since these are more suited to barleys of high germinative energy and proteolytic activity than to low nitrogen Californian and European barleys. It also takes into account the use of a high

proportion of unmalted maize or rice which yield no nitrogen to the wort and hence may be regarded as nitrogen diluents.

The suitability or otherwise of different types of barley for particular kinds of beer has been found by experience and may turn on structure, composition or enzymic activity. Provided that these, together with germinative energy, soundness, freedom from damage and mixture are favourably reported on, the total nitrogen of the grain is the safest available guide to brewing quality and potential extract. It is, however, impossible to state an optimum nitrogen content to cover all circumstances, since this differs in accordance with the type of beer, brewing methods and whether malt is to be used alone or in conjunction with other materials.

In certain grading systems used in Germany for two-rowed barleys intended for lager brewing, a nitrogen content of 1.6% on dry barley is taken as the optimum, with reduced marks for percentages above or below this. There is even a tendency to place the limit for high malting quality at 1.84% with the high nitrogen American barleys which are so much appreciated on account of the high enzymic activity that accompanies high nitrogen content.

A rough division of English barleys into grades on the basis of nitrogen content might be marked by 1.2–1.4%; 1.5–1.7%, and 1.8–2.1% on dry barley. Barleys in the first grade almost invariably have the best appearance, are the best malting barleys, and yield the highest extract and would cover most "pale ale" barleys. They would be selected for all malt beers of high or moderate gravity. It is usual to associate the nitrogen content with yeast nutrient qualities. 1.2–1.4% of nitrogen on dry barley is ample for this purpose in all malt top-fermentation beers of moderate gravity, but experience shows that a barley with higher nitrogen content is desirable for beers of lower gravity, particularly when unmalted grain or sugar, which contribute no nitrogen to the wort, are used and when the greater enzymic activity associated with higher nitrogen content is required.

There is frequently difficulty in obtaining mature barleys in England with a nitrogen content between 1.5 and 1.7% and barley containing more than 1.7% nitrogen on dry matter is usually difficult to modify on the malt floor and is generally disliked on account of its lower extract and tendency to give greyness in the beer. The maturity of high nitrogen barleys in this country is generally at fault and it is to this that most of their defects must be attributed. For this reason, as well as on account of their high extracts, low nitrogen barleys are to be preferred for stock beers whenever the gravity of the latter decides a sufficient pro-

portion of nitrogenous yeast nutrients in the wort. Properties of flavour, head formation and retention, associated with the higher protein content, indicate the use of barleys with 1.5 to 1.7% of nitrogen in lighter beers, provided they are mature and can be used without detriment to brilliance.

(65) Other Barley Constituents and Quality.

Although the most important influence on the malting quality of barley is at present attributed to the proteins it is possible that other constituents of the barley have effects that are at present only imperfectly realised. Starch contributes most to the extract, and thus in a very positive way to the market value of barley, and may favourably or unfavourably affect its malting quality, through variations in its colloidal state, but it is to the hemicelluloses that attention is beginning to be directed. It is very possible that additional light on the quality of barley will be gained through investigation of constituents of this nature, thus vindicating Brown's reference to the significance of the changes in the colloidal "gum" during malting.

REGULARITY IN THE COMPOSITION OF BARLEY

(66) Regularities in the Protein Composition of Barley.

Investigation of the composition of barley is hampered by uncertainty in regard to the exact nature of many of its constituents and by lack of reliable methods for their analytical determination. It has, however, been facilitated by the observation that the relative quantities of certain of its most important constituents are not subject to haphazard variation under the influence of soil and season but exist in well-defined relationship to each other. The existence of this regularity of composition was shown in the Institute of Brewing barley researches by analyses of a large number of Plumage-Archer barleys grown in different places and in different years under varying soil and climatic conditions, and the discovery by Bishop¹⁰ that the quantities of each of the individual proteins of this variety could be calculated in mature grain when its total nitrogen content was known, regardless of the conditions of soil and season which had influenced the total quantity or the manner in which it had reached the grain.

The results of some of the analyses on which this statement was based are plotted in Fig. 26, reproduced from Bishop's original paper. This shows that the quantity of each of the individual proteins increases with the total nitrogen of the barley, but not

REGULARITY IN PROTEIN COMPOSITION § 66

proportionally with the latter. It will be seen, when the total nitrogen is about 1.4%, that the hordein, glutelin and salt-soluble compounds are present in approximately equal quantities, but that the salt-soluble nitrogen increases at a much slower rate than the glutelin and hordein with increasing total nitrogen content.

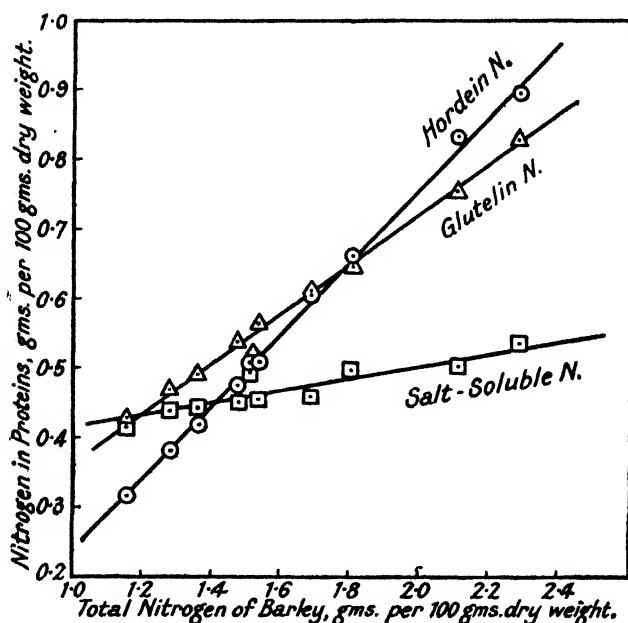


FIG. 26

QUANTITIES OF NITROGEN IN THE INDIVIDUAL PROTEINS OF PLUMAGE-ARCHER, AS PERCENTAGES ON DRY WEIGHT OF BARLEY

In Fig. 27 the hordein, glutelin and salt-soluble nitrogen are plotted as percentages of the total nitrogen content and found to fall on regular curves, so that the quantity of nitrogen in these three forms can be calculated for any of the Plumage-Archer barleys examined from its total nitrogen content. It will be observed that the glutelin nitrogen remains constant at about 36.5% of the total nitrogen, whatever the latter may be, but as the total nitrogen increases so does the hordein, while the salt-soluble nitrogen increases at a much slower rate, so that its percentage of the total nitrogen decreases in relation with the increasing proportion of hordein nitrogen. The hordein accounts for 27% of the total nitrogen, when this is 1.2%, and for 40% when the total nitrogen is 2.2%.

In analyses it is usual to express the quantities found as percentages by weight and it was on this basis that the regularities in protein composition were first detected. The natural unit

of the grain is, however, the single corn and the regularities are even more marked when the quantities of the individual proteins are calculated as percentages of the weight of a single corn or of 1,000 corns. Fig. 28 showing the relation between the hordein nitrogen and total nitrogen for a large number of English two-rowed barleys is a remarkable example of this regularity. It shows that the relation between the quantities of hordein and total nitrogen follows a definite rule and that the percentage of hordein can be calculated when the total nitrogen is known. The results plotted in this diagram are from analyses of several varieties of two-rowed barley and include immature as well as mature grain.

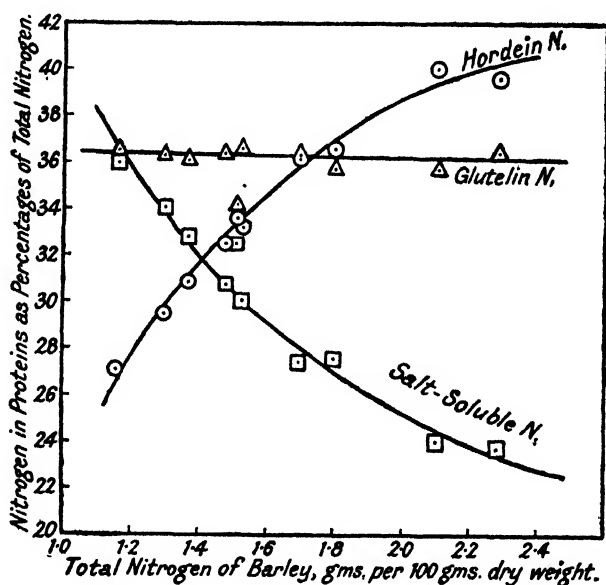


FIG. 27

PERCENTAGES OF NITROGEN IN THE INDIVIDUAL PROTEINS OF PLUMAGE-ARCHER BARLEY, AS PERCENTAGES ON TOTAL NITROGEN

(67) Meaning of Regularity.

The lack of proportionality between the individual proteins and the total protein of the barley has been noted in the analyses quoted, and it must be emphasized that "Regularity" is defined as "the character of having an arrangement which follows some rule." It does not mean fixed proportionality but covers the latter as one case of regularity. In reference to the composition of barley it means that the quantity of one constituent can be calculated from that of another when the rule governing their relationship is known.

(68) Effect of Variety on the Protein Relationships.

The analyses of Plumage-Archer barleys indicate that with any given nitrogen content there is a tendency for the individual proteins to settle down to an approximately definite equilibrium in the mature grain of one variety, but their relative proportions may vary considerably in different varieties. Thus, Bishop gave the following comparison between Plumage-Archer and Standwell barleys, both containing 0.5 gm. of nitrogen per 1,000 corns. The figures represent the nitrogen in the three protein fractions in grams per 1,000 corns.

	Salt-soluble	Hordein	Glutelin
Plumage-Archer	.. 0.175	0.140	0.185
Standwell	.. 0.24	0.18	0.18

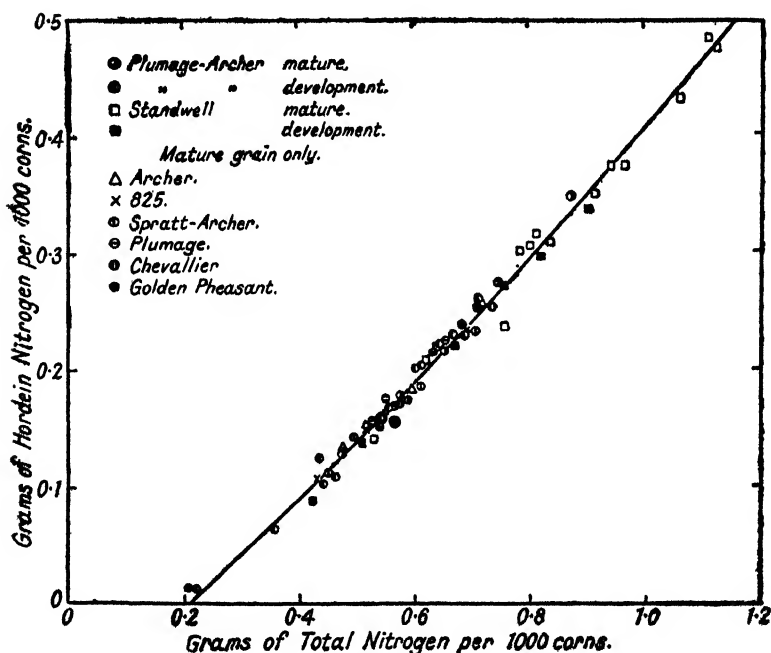


FIG. 28

RELATION BETWEEN HORDEIN NITROGEN AND TOTAL NITROGEN EXPRESSED AS GRAMS PER 1,000 CORNS

Bishop's conclusions in regard to regularity in the protein composition of barley and the existence of varietal characteristics have been confirmed by analyses of Danish (Hofman-Bang¹¹) and German barleys (Fink and Kunisch¹²).

The few available analyses of six-rowed barleys appear to show that the relationship between the proteins differs materially from

that existing in two-rowed barleys. They contain less hordein for an equal nitrogen content and in some cases a greater proportion of glutelin. How far this can be correlated with their special brewing qualities remains to be investigated. The analysis marked R & A is by Rose and Anderson, the others are by Bishop.

TABLE 9.—PROTEIN CONSTITUENTS OF SOME SIX-ROWED BARLEYS
(NITROGEN % ON TOTAL NITROGEN)

Barley variety	Total N.	Salt-sol. N.	Hordein N.	Glutelin N.
July (Manchuria)	1.957	25.3	34.6	40.1
O.A.C.21	1.725	25.3	34.9	39.8
O.A.C.21 (R & A) .. .	2.200	31.6	36.1	32.0
Atlas (Calif.)	1.389	33.4	26.9	39.7
Chilean	1.756	34.2	32.4	33.1

(69) Changes in the Proteins during Maturation of Barley.

It must be observed that the statements in regard to regularity in the protein composition of barley only apply to mature grain. Bishop¹³ stated that it was not safe to study it in barley less than a year old. The nitrogen percentage remains approximately constant throughout development, showing that nitrogen compounds, carbohydrates and other substances enter the grain in nearly constant relative proportions. Salt-soluble nitrogen is high in the early stages of growth. Glutelin increases steadily throughout and hordein most rapidly in the later stages. The relationships in mature grain are thus the results of the developmental sequence characteristic of the variety and, within each, there is a tendency for the proteins to settle down to a very definite equilibrium. Synthesis does not, however, keep pace with the rate of entry of nitrogen into the grain. Hence maturation changes occur, both before and after harvest.

Steely barleys usually contain more nitrogen and hence a greater quantity of hordein than mealy barleys, but the relationship between the hordein and total nitrogen is normal. The inferior malting quality of steely barleys is thus not a consequence of differences in the quantity of this protein. Changes in the proteins do, however, appear to be associated with the process of pre-harvest maturation and, according to the figures in Table 10 by G. Hofman-Bang,¹¹ are reflected by changes in the glutelin and salt-soluble proteins. These analyses show that while the proportion of hordein is approximately the same in immature and mature barleys, the salt-soluble nitrogen is higher and the glutelin proportion correspondingly lower.

TABLE 10.—PROTEINS OF BINDER BARLEY AT STEEP

	Salt-soluble protein	Hordein	Glutelin
Average % of proteins, 22 samples ..	3.53	3.41	2.67
Average % on total protein, 20 samples	36.5	36.2	27.3
Mean of two "immature" barleys ..	42.0	35.7	22.3

Fink and Kunisch also noted a small difference in the glutelin percentage on total nitrogen in the German barleys, according to variations in the weather conditions. This appeared to depend on the vegetative growth of the plant and corns. The glutelin was greater with stronger growth, particularly when the vegetative character of the cells persisted over a longer period and with later ripening barleys. A low percentage followed a dry period in the later stages of maturation and ripening, after rain during May and June or July.

(70) Changes in the Proteins during Storage and Drying of Barley.

It is generally accepted that there is a small loss of dry matter during drying and storage of barley. The loss is very variable but may amount, according to Miller,¹⁴ to between a few tenths and about 1% during drying and to a similar figure during a few months' subsequent storage. A slight increase in moisture content may arise at the same time from decomposition of carbohydrates, quite apart from absorption from external sources. Investigations with a barley which germinated only to the extent of 88% before kiln-drying and 98% afterwards led Windisch¹⁵ to the conclusion that the improvement was due to changes in the embryo and that little depended on the moisture content of the endosperm. It has also been suggested by Harrington¹⁶ that the improvement in germinative power is related to increase in the oxygen permeability of the husk.

Whatever may be the explanation of the improvement in the germinative activity, there is a slow change in the proportions of the proteins during storage. Hofman-Bang's analyses show that this may be considerable with some undried barleys, Table 11. These indicate decrease in the salt-soluble nitrogen accompanied by increase in the glutelin, the hordein remaining approximately constant. The changes in solubility may be due to alterations in the physical condition of the proteins, rather than to any chemical alteration. The rate at which they occur was found to depend on the moisture content of the barley and they were of little significance with barleys dried down to 11%.

TABLE 11.—CHANGES IN PROTEINS DURING STORAGE OF BARLEY
(UNDRIED BINDER BARLEY STORED AT 68° FAHR.)

		% Total protein	Per cent. on total protein		
			Salt-soluble	Hordein	Glutelin
A.	Before storage ..	9.84	35.4	35.7	28.9
	After 1 month ..	—	31.8	35.6	32.6
B.	Before storage ..	9.74	34.4	35.3	30.3
	After 1 month ..	—	31.4	35.3	33.3
C.	Before storage ..	9.50	34.7	35.7	29.6
	After 1 month ..	—	33.2	34.4	32.4
D.	Before storage ..	9.79	36.0	35.3	28.7
	After 1 month ..	—	32.7	36.1	31.2

It might be expected that the changes in the proteins brought about by drying would be similar to those which occur during storage with a greatly increased rate, but, according to Hofman-Bang, they are in the opposite direction. Instead of a change from salt-soluble protein to glutelin, there is an increase of the former and a diminution of the latter. This suggests that the improvement in malting quality of dried barley is due to the presence of more easily available protein which, under incipient germination, may be supposed to stimulate the formation or action of the proteolytic enzymes. The extent of the change produced during drum drying with air at 122° Fahr. is shown by Hofman-Bang's analyses in Table 12. The drying lasted 2–4 hours in two drums through which the hot air was passed in series, raising the temperature of the barley in the upper drum to about 113° Fahr.

TABLE 12.—EFFECT OF DRYING ON THE PROTEINS OF BARLEY

		Moisture	% Total protein	Per cent. on total protein		
				Salt-soluble	Hordein	Glutelin
A.	Undried ..	16.50	9.84	35.4	35.7	28.9
	Dried ..	12.12	—	37.1	36.0	26.9
B.	Undried ..	16.57	9.50	34.7	35.7	29.6
	Dried ..	12.08	—	38.2	35.6	26.2
C.	Undried ..	16.50	10.00	33.8	35.8	30.4
	Dried ..	11.70	—	36.2	36.1	27.7

(71) Regularities in the Carbohydrate Composition of Barley.

Some evidence has been obtained by Bishop and Marx¹⁷ that similar regularities exist among the carbohydrates of barley.

Lack of analytical methods preclude proof of this proposition by determination of the individual carbohydrates, but Fig. 29, constructed from analyses of Plumage-Archer, Spratt-Archer, Atlas and F 112 show, by the closeness with which the points fall on straight lines, how closely the quantities of certain reproducible carbohydrate fractions could be calculated when the type of barley and total carbohydrate was known. The fractions measured were (1) extract, (2) pentosans, representing hemicellulose, and (3) a fraction resistant to 0.5% H_2SO_4 and 0.5% NaOH, called the "insoluble fraction" and representing the cellulose and part of the lignin. It corresponds to about half the spent grains.

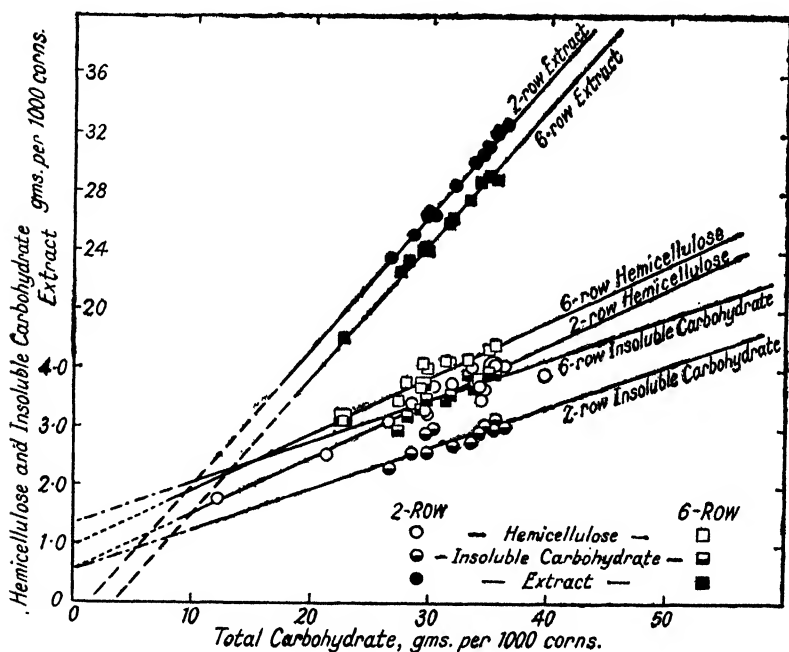


FIG. 29

CARBOHYDRATES OF TWO-ROWED AND SIX-ROWED BARLEYS

The diagram shows that the carbohydrate fractions measured rise regularly with increasing total carbohydrate. It also reveals differences between two- and six-rowed barleys that correspond with brewing properties. Thus the extract of the latter is less and the pentosan and "insoluble carbohydrate" greater than in two-rowed barleys with equal total carbohydrate content. It thus appears possible that the principle of regularity extends to the carbohydrates of barley. The limits of accuracy of the

methods make it difficult to determine varietal differences, but they do appear to exist. Thus Standwell gives a higher extract than Plumage-Archer and Spratt-Archer with an equal nitrogen content, while it contains less pentosans and "insoluble carbohydrate." Certain Manchuria type barleys analysed gave about 5 lb. per quarter more extract than Californian and other six-rowed barleys of Mediterranean type *at the same nitrogen content and thousand-corn weight*. On this basis the extract corresponds with that obtained from two-rowed barleys, although it is so very much lower weight for weight. This may point to very significant differences in the carbohydrate composition of Manchuria and Mediterranean barleys or may be due to a state of maturation in the high nitrogen Manchuria barleys rarely reached in other varieties when the nitrogen content is equally high. These questions await investigation, but they suggest that the morphological differences on which classifications are based could be replaced by broad differences in composition to form the basis of a rational classification of barleys in terms of their brewing properties.

A suggestive conclusion drawn by Bishop from the investigations described is that the grain of each variety of barley develops according to a definite pattern of chemical composition. The patterns differ only slightly in closely related varieties, but markedly between two- and six-rowed barleys. The varying patterns referred to are based on chemical composition, but, since some of the substances concerned are closely related to the structure of the grain, they should be revealed to a certain extent in such outward signs as the quantity of husk and have some influence on the morphological characters by which varieties are distinguished. It is not implied that barley of the same variety always succeeds in producing grain of the same chemical composition with the same brewing value, but, whatever the final composition and however it has been produced, an approximately regular relation is to be found between the quantities of various constituents of the mature grain of one variety. Further, no claim is made that the regularities found are as rigid as those existing, for example, among the elements of a chemical compound. Some degree of freedom or variation due to seasonal influences is to be expected in the components of living things, even though these are constrained to comply with a master pattern or quantity specification susceptible of analytical measurement. It has, however, been found possible to calculate the quantities of certain fractions from the specification, with an accuracy equal to that of the analytical methods available, in the case of a few varieties for which the specifications have been worked out.

(72) Implications of Regularity on Barley Quality.

The implications of the fundamental principle of regularity in barley composition are far-reaching and can be applied in several ways in malting and brewing. If, for example, the malting quality of barley actually depends on the relative proportions of the individual proteins or if the quantity of hordein provided a good criterion, as has been suggested by Munro and Beaven,¹⁸ it would be no longer necessary to determine the percentage of individual proteins, since these are related very closely to the total nitrogen content in a mature barley. While the total nitrogen depends mainly on soil and season and to a smaller extent on variety, manuring and other cultural conditions, the percentage of the total nitrogen present in each of the individual proteins depends on the variety, maturity and total nitrogen content. The latter is almost settled before the end of June in England and depends on the relative rates of nitrogen uptake and carbohydrate formation by the leaf during the early period of growth, but July and August weather govern the final stages of maturation and physiological condition which are so important in regard to malting quality.

Maturity would thus correspond with attainment of the normal composition characteristic of the variety at the particular nitrogen content determined by the soil and weather during the growing season. Attainment of this normal composition would also seem to be associated with the colloidal state of the constituents involved. This is in a state of flux during growth and maturation and, if arrested prematurely or before the quantitative relations are fixed as required for the highest germinative activity, the malting quality of the barley must suffer.

Two processes may be distinguished in the ripening of grain: (1) transfer and storage and (2) synthesis of insoluble, non-diffusible reserve material of high molecular complexity from the soluble substances. Transfer and accumulation outweigh synthesis at first. There is an increase in corn weight, with a rise in the percentage of low molecular substances. This is followed by approximate parallelism in the two processes until the grain becomes yellow. Then condensation begins to outweigh accumulation. The percentage of the more soluble substances decreases and that of the more complex rises until, at ripeness, the former ceases, but increase in high molecular substances still goes on to dead ripeness and even during post-harvest maturation.

Light, moisture and warmth are the governing factors on which correct adjustment of the composition of the grain and its quality depend. Early drought and heat, or any other abnormality, are

bound to lead to reduced malting quality in barley. The protein investigations mark an important step in elucidating the chemical changes associated with ripening and maturation. Their implications cannot as yet be fully interpreted, but it may be hoped that they will lead to accumulation of information on the composition of barley that will be helpful in determining its malting quality and utility for brewing.

POTENTIAL EXTRACT OF BARLEY

(73) Composition of Barley and Potential Extract.

One of the most important aspects of the composition of barley from the brewer's point of view is its relation with the extract obtainable after malting. It has generally been assumed that the protein of barley affects the available extract, or that which should be obtained from the malt, by direct replacement of carbohydrates. This, however, is not strictly true. An increase of 0.1% in the nitrogen content of barley means an increase of about 0.6% of protein and a corresponding decrease in carbohydrates. About one-third of the protein becomes soluble in the wort after malting and contributes to the extract, but, despite this, each 0.6% of protein decreases the extract of otherwise similar malts by about 1%, when the latter is determined by the English method with coarsely ground grist. It is probable that some of the starch is locked up in a matrix of resistant protein and is not extracted when the grist is coarsely ground. This sealing up no longer occurs when the extract is determined with finely ground grist, but the reduction is still greater than can be accounted for by displacement of carbohydrate by insoluble protein, even when allowance is made for loss of nitrogen during malting, which is actually slight when expressed as a percentage of the malt, since a greater quantity of carbohydrate is lost at the same time by respiration. It might also be expected that greater extract would be obtained from larger corns, since these would contain proportionally less husk and germ than smaller corns.

The analytical data accumulated in the course of the Barley Researches of the Institute of Brewing made possible a statistical examination of the relations between the nitrogen content and thousand-corn weight of barley and the extract of the malt made from it. Bishop¹⁹ found that nitrogen content and corn weight both affect the extract of the malt and that the relation could be expressed in the form of an equation from which the extract could be calculated with good approximation when the nitrogen

content and thousand-corn weight of the barley were known. This examination applied in the first instance to Plumage-Archer barleys only. It was later extended by Bishop and Day²⁰ to other varieties and it was found that the nitrogen content and thousand-corn weight had similar, if not the same, effects on the yield of extract in all the varieties studied. That is to say there are constant differences between varieties in their extract yields at corresponding nitrogen contents and thousand-corn weights. It was therefore possible to construct an equation in which the nitrogen and corn weight factors were the same for all varieties, and in which the only necessary adjustment was in a constant term, referred to as the varietal constant. This equation was estimated to apply to the barleys examined with a standard error of ± 0.8 lb. The error is liable to be greater with low grade or unsound barleys and it would appear that some factor related to the physical state or vitality of the barley was missing from the equation.

(74) Prediction of Extract.

The equation proposed by Bishop and Day was

$$E = A - 10.5 N + 0.2 G$$

in which E is the predicted extract of the dry malt in Brewers' pounds per quarter of 336 lb., determined by the Institute of Brewing standard method. N is the nitrogen content as a percentage and G the thousand-corn weight in grams of the barley, both expressed on barley dry weight. A is the varietal constant. This varies slightly with the barley variety. The following values were found to give the most correct results for the particular barleys examined. English :

Standwell	110.0
Beaven's Archer	109.2
Webb's Sunrise	109.2
Chevallier	108.9
Spratt-Archer	108.9
Plumage-Archer	108.3
Plumage	108.2
Archer	108.2
Goldthorpe	107.8

The incorporation of a varietal constant in the equation stresses the differences in composition between barleys of different varieties, and their establishment by the results of a sufficient number of analyses shows that these differences are characteristic of the varieties. They are, however, small in closely allied varieties

and, since the variety of barleys is in many cases unknown, it is necessary and sufficiently accurate for practical purposes to take a mean value for English and other values for the various types of foreign barley. Among the latter the barleys of Mediterranean type, of which Californians are typical, have considerably lower varietal constants than barleys of the Manchuria type when both are malted by English methods. Approximate varietal constants for commercial use are given in Table 13.

TABLE 13.—APPROXIMATE VARIETAL CONSTANTS FOR COMMERCIAL USE

Barley				Varietal constant A
English	108.5
Californian	103.0
Manchuria	107.0

Comparison of predicted extracts with those actually obtained is very valuable either in the valuation of barley or for the interpretation of malt analyses, even when the barley itself is not available. The equation with the constants given in Table 13 has been applied by the writer to a very large number of malts made by many maltsters and found to give results of remarkable accuracy, though the constant is subject to seasonal influences and may be 110 for English barleys in a season when they modify very readily. The method is to be preferred to any other for determining the potential extract of barley and serves in the control of malting by showing whether the extract actually obtained is what should be expected from the barley.

The extract obtainable from any barley varies with the degree of modification and consequently the equation and the constants given can only apply accurately to malts made under comparable conditions. It is therefore advisable to carry out a number of analyses of barleys and their malts before the prediction equation is made use of in any particular maltings in order to make sure that the constants apply with sufficient accuracy. No other adjustment is likely to be necessary than an increase or decrease of the varietal constants by 0.5 or 1.0 at most. Very mellow barleys usually give higher extracts than those calculated from an average varietal constant and stubborn barleys a lower extract, since the former are likely to be proportionally more fully modified than the latter. An unusually high percentage of dead corns in the barley or of immature grain, giving undermodified malt, will throw the results out rather badly and discrepancies occur with badly screened barleys containing an undue percentage of small corns:

The varietal constants and the various factors in the equations given were all derived from analyses made by the Institute of Brewing method and any variation in details of the extract determination would necessarily alter them. It must also be remembered that all the figures for extract of the malt, thousand-corn weight and nitrogen content of the barley are calculated to moisture-free material. If finely ground malt is used for extract determination the result is usually 1 to 3 lb. higher, the increase varying with the degree of modification. A more accurate equation might be constructed for finely ground malt, but it would tend to eliminate variations due to the degree of modification, which the original equation shows up, and thereby reduce the value of the method for appraising the malt. The following equation is suggested for use with the Congress method of analysis, using finely ground grist. The extract and nitrogen content are expressed in the manner usually adopted on the Continent, as per cent. Plato and Protein % (P), all calculations being made on the dry basis.

$$E = A - 0.85 P + 0.15 G$$

83 and 79 may be used as approximate varietal constants for two-rowed European and six-rowed Californian barleys in place of 108.5 and 103 for the Institute of Brewing analyses. Examples of predictions and analyses are given in Table 14.

TABLE 14.—PREDICTION OF EXTRACT

Barley malted	On Dry Barley		Extract of Dry Malt				P.S.N. % of N. Inst. Brew.
	N	G	Inst. Brewing lb.		Congress % Plato		
			Predicted	Analysis	Predicted	Analysis	
English ..	1.406	36.5	101.0	101.3	81.0	81.2	37.0
„ ..	1.510	36.0	99.8	99.7	80.4	80.0	35.4
„ ..	1.657	40.0	99.1	98.5	80.2	79.9	29.3
Californian	1.592	41.5	94.6	94.5	76.8	76.6	29.8
Pale lager..	1.640	38.0	98.9	99.2	79.0	79.8	30.0
„ ..	1.976	38.5	97.7	97.1	78.5	78.6	27.4

The greatest difficulty in making use of prediction methods is that of obtaining representative and comparable samples from large bulks of barley and malt. The accuracy of predictions is also limited by unavoidable errors of analysis in nitrogen content, thousand-corn weight, moisture percentage and extract. On the other hand use of the equations provides an excellent method of checking analyses and detecting errors. The presence of dead corns necessarily increases the difference between the actual

extract of a malt and that predicted from the barley. Bishop²¹ calculated an equation for estimating the extract on "raw barley," in which allowance was made for the percentage of dead corns (X) and of moisture, DM representing the dry weight of 100 grams of the raw barley of which the extract in brewers' pounds per 448 lb. is given by R. Varietal constants given for this equation were 136 and 137 for narrow- and wide-eared English barleys respectively and 129 for Californian and similar barleys. Nitrogen content (N) and 1,000-corn weight (G) are referred to the dry weight of the barley. This equation is

$$R = \left[C - 15 N + 0.2 G + (1 - 0.3 X) \right] \times \frac{DM}{100}$$

Bishop²² was also able to construct an equation by which the extract could be calculated from the total nitrogen content (N) and the "insoluble carbohydrate" (I). This avoids the use of a varietal constant and may thus be useful with barleys of unknown variety and particularly with husky six-rowed barleys, but has no advantage over the nitrogen equation for two-rowed barleys of known variety. The equation was :

$$E = 134.7 - 9.0 N - 2.8 I$$

(75) Direct Determination of the Extract of Barley.

Several methods for direct determination of the extract of barley by gelatinisation followed by diastatic conversion are in use. Some of these give results which correspond fairly closely with the extract of the malt, but they have no advantages over the methods of calculation from nitrogen content and thousand-corn weight. They generally involve rather lengthy analytical processes, gelatinisation by boiling under pressure being adopted in some of them. In others the liquefaction is secured by use of the bacterial enzyme "superclastase," this being followed by saccharification with diastase preparations. A method which has been found to give good results is included among the analytical processes collected in Vol. II.

(76) Valuation of Barley from Potential Extract and Nitrogen Content.

As a result of the investigations on the proteins of barley which have been outlined, Bishop²¹ has suggested a scheme of barley valuation based on the potential yield of extract and of soluble nitrogen. These are no doubt the essential requirements in barley that can be assessed by analysis. On them its brewing quality largely depends, but there are other qualities depending

on maturity, regularity and freedom from damage which cannot be measured by analytical methods, even when these are completed by germination tests. The scheme should therefore be considered as complementary to hand examination but, providing the results of the latter are in every way satisfactory, it affords a means of bringing valuation into closer relation with brewing quality than is possible by hand examination alone.

The scheme is intended to apply to barley as received at the maltings and consequently must take cognizance of the moisture content of the "raw barley," for it is obvious that if two barleys were otherwise absolutely the same a lower moisture content in one would increase the quantity of malt or extract obtainable from it and consequently its market and brewing value. The potential extract, or extract which should be obtained when malted under standard conditions, is therefore calculated on the raw barley to allow for the effects of varying moisture content and malting loss. In good samples of barley the effects of variations in germinative activity can be neglected and a simplified equation based on that given in Section 74 is suggested for arriving at the potential extract. This is

$$R = C \times \frac{DM}{100} - 15N,$$

in which R is the potential extract of the raw barley ; DM is the dry matter percentage of the barley, i.e., 100 less the moisture content, and N, the percentage of nitrogen on sample, not in this case on dry matter. C is the varietal constant, for which values appropriate to this equation were found to vary from 147 for Standwell, Kenia and Isaria to 137 for Californian barleys, being 145 for most English wide-eared barleys and 144 for narrow-eared.

TABLE 15.—CLASSIFICATION OF ENGLISH BARLEYS ACCORDING TO POTENTIAL EXTRACT, NITROGEN CONTENT AND USE

Class	Potential extract raw barley	Nitrogen content % on dry	Original gravity of beer
1	— 106	— 1.35	— 1080
2	105.9 — 104	1.35 — 1.45	1079 — 1060
3	103.9 — 102	1.40 — 1.50	1059 — 1050
4	101.9 — 100	1.45 — 1.55	1049 — 1040
5	99.9 — 98	1.50 — 1.60	1039 — 1030
6	97.9 — 96	1.55 — 1.65	1029 —
Reject	95.9 —		

The proposed classification would divide English barleys into six malting classes and a reject, according to Table 15, in which

they are graded according to their potential extract. The corresponding nitrogen content given in the second column is only approximate. It would hold if the barley contained the normal percentage of moisture, around 15%, but a low nitrogen barley would be dropped a class or two if it was high in moisture content.

A similar scheme of classification, but simplified to include only four classes of malting barley, was proposed for foreign barleys. This is admittedly only tentative as it is based on the very restricted number of samples analysed in the Institute of Brewing investigations, and no doubt requires modification to cover the bulk of commercial imported barleys. It is, however, sufficiently suggestive to indicate the lines along which a comprehensive scheme of barley valuation might be constructed. The proposed extract ranges are given in Table 16.

TABLE 16.—CLASSIFICATION OF FOREIGN BARLEYS

Class	Extract ranges on Raw Barley, Brs'. lb. per 448 lb.				
	Indian	Californian Chilean Brewing Australian Cape	Canada, Western	Foreign two-rowed	Simplified English classification
A	— 109	— 105	— 103	— 109	— 105
B	108·9 — 106	104·9 — 102	102·9 — 100	108·9 — 106	104·9 — 102
C	105·9 — 103	101·9 — 99	99·9 — 97	105·9 — 103	101·9 — 99
D	102·9 — 100	98·9 — 96	96·9 — 94	102·9 — 100	98·9 — 96
Reject	99·9 —	95·9 —	93·9	99·9	95·9

The extract figures for six-rowed barleys may appear high, but this is because it is natural to think of extract on malt. With English barley in normal years, extract on barley and malt are approximately the same, but foreign six-rowed barleys with their lower moistures and malting losses yield as much or more extract per quarter of raw barley as does English, despite the lower extract on malt. The high extract on the foreign two-rowed barley is also due to the low moisture content of the raw barley. The extract is in each case calculated on a quarter of the material, that is on 448 lb. of barley or 336 lb. of malt.

448 lb. of English barley containing 16% of moisture and suffering a malting loss of 11% on dry matter would yield 341·7 lb. of malt with 2% moisture. If this had an extract of 98 lb. per quarter of 336 lb. the potential extract of the raw barley would be $\frac{98 \times 341 \cdot 7}{336} = 99 \cdot 7$ lb. per quarter of 448 lb.

On the other hand a six-rowed foreign barley with a moisture content of 11% and a malting loss of 9% would yield 370.2 lb. of malt with 2% moisture. If this had an extract of 92 lb. the potential extract of the raw barley would be

$$\frac{92 \times 370.2}{336} = 101.4 \text{ lb. per quarter of 448 lb.}$$

The suggested scheme also provides a guide to the use of the barleys in brewing based on the requirements of assimilable nitrogen in the wort. It is assumed that the total nitrogen existing in the boiled wort, the permanently soluble nitrogen, is a good measure of the yeast-feeding properties. This assumption rests on experimental evidence that the principle of regularity of composition extends also to wort, a proposition that is dealt with in a later chapter. Here it may be assumed that the total nitrogen content of the barley is a satisfactory measure of the potential soluble nitrogen in the wort, which is shown to be the case in the chapter on malt. Extension of the scheme to the classification and use of malts is also described later, when the implication that the brewing value of barley depends on the potential soluble nitrogen as well as on the extract will be made clearer.

(77) Summary and Extension.

The nitrogen content of barley provides the most reliable analytical criterion at present available of its malting quality, and also of its suitability for any particular type of beer or brewing process. The requirements for brewing are so varied that it is impossible to state an optimum nitrogen content to cover all cases. The best rules for guidance in the selection of barley from samples of the particular type preferred are :—

- (1) Insist on maturity. Both malting and brewing quality suffer, whatever the nitrogen content, if the barley has not normally and evenly matured or if it has prematurely dried off. Given maturity, soundness, vitality, regularity, and freedom from damage, judgment of the malting quality or suitability for brewing under the given conditions may be based on the nitrogen content.
- (2) Select barley of the lowest nitrogen content compatible with the required converting power and yeast nutrient properties, obtaining in this way the highest possible extract with the greatest protein stability.
- (3) Judiciously balance the nitrogen content of the barley with the proportion of carbohydrate adjuncts employed to yield an adequate percentage of nitrogen in the wort solids. This point will be amplified later and must be considered in relation

with the gravity of the beer in order to supply a sufficient quantity of nitrogenous yeast nutrients.

(4) Select a variety that comes to maturity and malts easily at the nitrogen content desired.

The principle of regularity in the composition of barley has been found to have valuable practical applications, among which is the possibility of calculating the potential extract of barley from determination of its nitrogen content, moisture and thousand-corn weight by the following equations based on English and Continental methods of analysis respectively :

$$E = A - 10.5 N + 0.2 G$$

in which A is represented by 108.5 for English barleys, 103.0 for Californian and other six-rowed Mediterranean varieties, and 107.0 for Manchuria barleys.

$$E = A - 0.85 P + 0.15 G$$

in which 84 and 79 may be taken as approximate varietal constants for European two-rowed and six-rowed Californian barleys respectively.

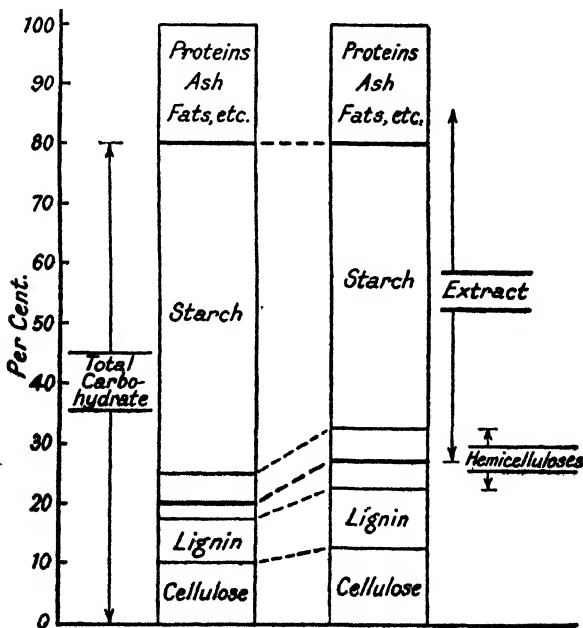


FIG. 30

DIAGRAM OF COMPOSITION OF HIGH AND LOW EXTRACT BARLEYS WITH SAME NITROGEN CONTENT

Barleys of the same variety with equal nitrogen content and

thousand-corn weight give the same extract when malted in the same manner, but the relative proportions of extract-yielding material and nitrogen may be quite different in other varieties. The varietal constants in prediction equations must consequently be appropriate to the varieties. This is illustrated in Fig. 30, in which differences in the carbohydrate composition of high and low extract barleys, e.g., two-rowed and six-rowed, are shown diagrammatically.

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AN INTRODUCTION
TO THE BIOCHEMISTRY OF MALT
AND WORT

CHAPTER VI

COLLOIDS AND HYDROGEN IONS

COLLOIDS

(78) Biochemistry.

The instinct that has guided brewers in their dealings with barley and yeast has been developed through generations of experience of cause and effect and had nothing in its origins to do with science. It has, however, gained immensely since knowledge of some of the reasons for what is done and what happens have been grafted on it. Never has more attention than now been given to science in connection with brewing, but there is always the danger that each new line of thought and each fresh discovery may distract attention from the many others that help to make up the scientific basis of brewing. It does not do to be attracted by novelty away from the fundamentals, which may be thought old-fashioned merely because they have guided practice for many years. No other art is based on a more delicate interplay of forces, so many of them controlling the ordered development of living things, and it is only of very recent years that the science of biochemistry has risen to study the laws that govern them. Its discoveries have crowded one after another during those years, but undue weight attached to one has led, and will continue to lead, to errors when attempts are made to put it into practice without due consideration of other factors or realisation of the true balance between them. Physics is coming into its own, alongside chemistry and biology, in the attempts to unravel the mysteries of life and living things, and in many ways forms a link between them through study of the properties of matter in the colloidal state. It is consequently desirable to describe in a simple manner some of the general properties of colloidal systems which have direct applications in brewing, before dealing with the chemical nature of their constituents.

It is assumed that the reader is familiar with elementary general organic and inorganic chemistry, but, as a brewer, is confronted in a very intimate way with certain intricate branches of biochemistry, which require consideration from a rather specialised point of view to relate them to brewing operations or to

§ 79 BIOCHEMISTRY OF MALT AND WORT

reactions encountered in its various processes. The manner of approach adopted involves, in some cases, a complete reversal of the logical sequence from simple to complex and can only be justified by familiarity with the simpler branches of chemistry and because brewing is essentially a process of simplification from colloidal materials, through sugars, to alcohol and CO_2 .

(79) The Colloidal State.

Such immense molecules as those of starch and some of the proteins, with molecular weights 600 times or more greater than that of maltose, suggest the possibility of properties of quite another order than those of crystalline sugars, properties dependent on the size of the molecules or the surface of the particles, rather than on their chemical constitution or constituent elements. The existence of such properties seems to be implied in the differentiation which Thomas Graham made in the middle of the nineteenth century between substances which were able or unable to diffuse from their solutions through a parchment membrane into water. He called these two groups of substances crystalloids and colloids respectively, and, though his classification was soon found to be unsatisfactory because many substances can exist in both forms, the conception of properties dependent on particle size holds and is of immense importance in brewing. In every stage from malting to fermentation there is a reduction in size and molecular complexity from starch and proteins to simple sugars and amino-acids which can pass through the cell membrane of yeast.

It is now recognised that the term colloid cannot correctly be applied to a substance but can only be used to describe the state in which it exists under given conditions. It implies a state of matter in which the particles of a substance are dispersed among those of another, producing a system characterised by special properties which alone will indicate whether the substance in question is in the colloidal or crystalloidal state. Diffusibility through a suitable membrane still remains one of the simplest methods for deciding whether a substance dissolved in a liquid exists in a state of true solution or in a state of colloidal dispersion, but there are other criteria by which colloidal systems may be distinguished from true solutions. Among these are the very small effects which the dispersed substance has on the osmotic pressure, boiling point or freezing point of the liquid, properties which all point to enormous molecular weights.

(80) Size of Colloid Particles.

The simplest explanation of differences in the rate of diffusion

from water through parchment membranes is to be found in variation in the size of the particles. Ions and molecules are believed rarely to exceed $1\text{ m}\mu$ in diameter, but measurements of the size of typically colloidal substances have given much larger figures. Svedberg came to the conclusion that egg albumin had the smallest particle size of any protein he examined, about $4.34\text{ m}\mu$ in diameter, with a molecular weight in the neighbourhood of 34,500. Certain plant proteins gave results suggesting a molecular weight of about 210,000.

These figures may be compared with the limits of microscopic and ultramicroscopic vision, for which purpose the units of size commonly adopted are the *micron*, $1/1000\text{ mm.}$, represented by μ , and the *mille micron*, $1/1000$ of a micron or one-millionth of a millimetre, represented by $\text{m}\mu$ or $\mu\mu$. Visibility with transmitted light and the best microscopes begins at about $0.2\text{ }\mu$. Particles of smaller size, down to about $5\text{ m}\mu$, are invisible with transmitted light, but can generally be detected by ultra-microscopy, that is when illuminated by oblique light accurately applied, by a dark ground illuminator for example. Some particles larger than $5\text{ m}\mu$ may, however, remain invisible if their optical properties differ little from those of the liquid in which they are dispersed. The so-called *Tyndall effect*, produced by scattering of light from ultramicroscopic particles, provides one example of the different effects of transmitted and oblique illumination. A brilliant beer may in this way appear opalescent when a strong beam of light is passed through it transversely to the line of sight.

(81) Definition of Colloids.

The modern definition of the colloidal state is based on this conception of particle size and liquid systems are referred to as colloidal when they contain particles varying in size between 5 and $200\text{ m}\mu$. It should be noted that these limits are quite arbitrary and there must be an upper zone where properties characteristic of the colloidal state shade into those of microscopically visible or massive particles, and a lower zone in which ultramicroscopic particles behave in many respects as if they formed true molecular solutions. Thus the particles of crystalline egg albumin behave in many respects as if they formed true molecular solutions, while bacteria and other particles of similar size may act like colloidal micelles or particles. A concrete conception of the meaning of these measurements may be gained by comparison with the dimensions of a yeast cell, which is approximately $8\text{ }\mu$, $8,000\text{ m}\mu$ or $1/3000$ of an inch in diameter.

(82) Colloidal Systems.

Though the colloidal state may be defined by the size of the particles of the substance involved, it also implies their dissemination among those of another substance, producing colloidal systems of various types comprising :—

Liquid in gas—mists, clouds and sprays.

Solid in gas—smoke.

Gas in liquid—foam of beer.

Liquid in liquid—emulsoids.

Solid in liquid—suspensoids.

Gas in solid—pumice.

Liquid in solid—some minerals.

One component of the system is *dispersed*, the other is the *dispersion medium* and these constitute respectively the *disperse phase* and the *continuous phase*. When the continuous phase of a colloidal system is a liquid the system is referred to as a *sol*, to distinguish it from a true solution which it resembles in appearance. More or less rigid colloidal systems are referred to as *gels*. The dispersed particles are frequently called *micelles*, and the fineness of their division, known as the *degree of dispersion*, has a predominant influence on the properties of the system. The dispersion of colloidal particles in the dispersion medium, which is brought about by processes of *peptisation*, demands addition of energy to the system, since the substance dispersed as micelles has a much greater energy content than it had when in mass. In the case of such substances as gelatin it is only necessary to add energy in the form of heat to obtain a sol in water. In other cases it is necessary to add a peptising agent, which is adsorbed on or forms a soluble compound with the substance to be dispersed. If dispersion is sufficiently profound, true solution occurs, but if the molecules of the solute cling together firmly they may form particles of colloidal dimensions. The result is a separation of units, rather than a division of molecules as in true solution.

Ostwald divided colloidal systems into *emulsoids* and *suspensoids*, according as the dispersed particles were liquid or solid. Proteins are solid substances, but it is not certain whether they remain as such when dispersed or become liquid through the large amount of water they take up. *Emulsions*, such as are formed when oil is dispersed in water, may contain particles much greater than of colloidal dimensions. Division into *lyophilic* and *lyophobic* systems, according as the dispersed particles have an affinity or otherwise for the medium, is in many ways preferable to Ostwald's classification. In lyophilic systems the phases are more or less

mutually soluble one in the other. In lyophobic systems neither phase is soluble in the other.

PROPERTIES OF COLLOIDAL SYSTEMS

(83) Properties Dependent on Active Surface.

The colloidal zone may be considered as transitional, in that particle movement and active surface are both moderately great. Both increase with diminution in particle size, and the kinetic activity of particles of molecular size becomes disruptively great. Above colloidal dimensions the kinetic activity is small, even when compared with the reduced surface energy. *Surface tension*, which has important effects on the properties of beer, may be defined as the force operating to hold a surface together. The surface tension of a liquid is measured by the tensile force in dynes exerted across any centimetre line on its surface. This causes the surface film to behave as a stretched elastic membrane, with different physical properties from those of the liquid below and a constant tendency to reduce its area. Examples are :

	<i>S.T. dynes /cm.</i>	<i>Temp. °C.</i>
Water	72.5	20°
Ethyl alcohol ..	22.0	20°
Acetic acid ..	23.5	20°

The surface energy may be measured by the work necessary to increase the surface by 1 sq. cm. and can be expressed in ergs per sq. cm. It is the product of the surface tension and the surface area. Like all other forms of energy it tends to do work and become a minimum. Since the surface tension of a pure liquid is definite, the only way to reduce its surface energy is to reduce its surface. If the liquid is a solution, its surface energy may be reduced by concentrating the solute at the surface. Hence a dissolved substance must concentrate at the surface of the liquid if it thereby reduces its surface tension, as it usually does.

(84) Adsorption.

This is a property of surfaces to which reference is constantly made in every phase of brewing. It is defined as the fixation of a substance at an interface, or the tendency of a substance to concentrate at the surface of another. Examples are found in the tendency of a dissolved substance to concentrate at the surface of a liquid, this being an interface with air, and also in the tendency to coat the surface of a solid immersed in the liquid. Substances which reduce surface tension in this way are "surface active." In

§ 85 BIOCHEMISTRY OF MALT AND WORT

analogy with surface tension, a colloidal system may tend to diminish its interfacial energy by bringing into the interfacial film substances which lower the interfacial tension. These would consequently be adsorbed there. The great surface energy of colloidal micelles causes them to exhibit adsorption phenomena in a very high degree, without necessarily involving chemical combination. In some cases electrical forces appear to cause the adsorption. Thus, certain colloidal fungicides penetrate the water film on a hop leaf and adhere firmly to its surface, being held by the negative charge on the leaf. Similar conditions may possibly cause the attachment of colloidal material to the surface of a fermenting vessel or coat the surface of yeast cells with protein and resin.

(85) Filtration.

Adsorption phenomena play an important part in the filtration of beer, and cause the removal of colloidal colouring matters and substances which contribute to the properties of palate-fulness and head-retention. Graded collodion membranes can be prepared and calibrated for ultra-filtration. Those with pores between $0.5-1.0 \mu\mu$ will remove bacteria and sterilise protein suspensions, but allow the protein to pass with a minimum loss due to adsorption. Finer pored membranes are made which will not permit the colloidal micelles to pass. Elford and Ferry¹ have shown by experiments with these that the adsorption of various proteins is greatest over a fairly wide range of p_H in the neighbourhood of the isoelectric point of the protein in 1% saline, the filtration end point for serum globulin, for example, being with pores of about $25\mu\mu$. For serum albumin there is a sharp peak of poor filtrability between p_H 4.2 and 7, where the end point values of average pore diameter lie far above the molecular size ($5.4 \mu\mu$), with a gradation on either side to good filtrability. The large peak of adsorption in the isoelectric region was found to be the same whether the adsorbent be collodion, quartz, kieselguhr or kaolin, suggesting that it is due to adsorption of protein on protein and not of protein on adsorbent. This corresponds with the tendency of proteins to aggregate at the isoelectric point and results in blocking the pores of the filter. The conditions within the pores are exceptionally favourable to the formation of protein aggregates, owing to the frequency of collisions in the limited space. The aggregation of colloids and blocking of filter pores in beer filtration may possibly be reduced in degree by the presence of salts which tend to peptise proteins or oppose their aggregation, but it is a factor that has to be seriously considered in filtration, whether it be by pulp or kieselguhr.

The great importance of adsorption in colloidal systems is due to the immense specific surface of the particles. The initial phase of reactions in which colloids take part appears to be due to surface adsorption, of which examples may be found in the adsorption of tannin on proteins and in the action of enzymes. The adsorption of tannin on coagulated proteins may be affected by the size of the pores in the gel of the latter. They may be so fine that the large molecules of the sol particles cannot penetrate into its interior and thus only affect the external layers.

(86) Foams.

Foams consist of a system of gas bubbles dispersed in a liquid, a gaseous disperse phase in a liquid dispersion medium, but the particles of the former are rarely of colloidal dimensions. Pure liquids do not form a foam when shaken, the presence of molecular or colloidal particles in solution or dispersion is essential. The dispersion medium, or liquid which separates the bubbles, may be of extreme tenuity. Its surface has in fact been enormously increased in opposition to the surface tension, which, like other forms of energy, constantly tends towards a minimum. This may be achieved by reducing the surface and, hence, a bubble assumes a spherical form. The surface energy of solutions may also be reduced by concentration of the component of lowest surface tension in the surface. This is the general course of events in foam formation, as, according to Gibbs and Thomson's law, in any solution the substance with the lower surface tension is concentrated at the surface. A 10% soap solution has a surface tension of only 25 dynes per cm., while that of water is 73 dynes. Hence soap molecules accumulate at the surface and form an almost rigid film. The rigidity of the films is materially influenced by the structure of the surface active substances. Long polar molecules arrange themselves in a definite direction. Thus the carboxyl group in soaps has a strong affinity for water, while the hydrocarbon chain is hydrophobic and would tend to extend above the water surface, the carboxyl group being immersed.

The stability of foams depends also on certain other properties of the liquid and of the gas. The liquid must not evaporate rapidly and should have a relatively high viscosity to prevent it draining off the bubble film. Ability to form solid surface pellicles to strengthen the film, slow evaporation and sufficient viscosity are the important factors in the formation of foams. Dispersions of many colloids such as proteins and gums admirably fulfil these requirements of the disperse phase. Wort and beer have a sufficiently low vapour pressure to avoid rapid evaporation, while the protein and other colloidal particles reduce the surface

§ 87 BIOCHEMISTRY OF MALT AND WORT

or interfacial tension by collecting at the interface of gas and liquid, where they form a resistant skin around the bubble. The surface tension of beer is about 48 dynes per cm. It is probable that proteoses are active in foam formation in wort, but it has been claimed that the "gums" of barley are mainly concerned in increasing the viscosity of the liquid.

The properties of the gas are also of great significance to the stability of the foam. If the surface tension is constant, the pressure in a bubble is inversely proportional to its diameter, and the gas tends to pass from smaller to larger bubbles. At constant pressure, the size of the bubbles is proportional to the surface tension. As bubbles ascend through a liquid a film of the surface active substance accumulates at their surface. The smaller the bubbles, the more slowly they rise and consequently the greater will be the concentration of surface active substances and the more stable the film. The liquid will also drain from the surface of small bubbles more slowly than from large. Since the pressure is greater in the small than in larger bubbles, there is a tendency for the gas to diffuse from the former into the latter and this diffusion will be more rapid according to the solubility of the gas. If the gas dissolves in the liquid film it can more readily pass to another bubble. Hence bubbles containing the almost insoluble oxygen or nitrogen are more stable than bubbles containing CO_2 . These general properties of foams will be more particularly dealt with in the sections on the foaming properties of beer.

(87) Electrical Phenomena in Colloidal Systems.

The dispersed particles in a colloidal system behave as if they carried a positive or negative charge and if, for example, an electric current is passed through a sol contained in a tube, the dispersed substance may be observed to concentrate at one end of the tube or the other as the particles migrate towards the negative or positive pole, a phenomena known as *cataphoresis*. Markedly amphoteric particles, such as those of proteins, may move in either direction according to the reaction of the medium, towards the negative electrode in acid liquids and towards the positive electrode when the medium is alkaline. There is, however, a certain p_H value, characteristic of the protein, at which no migration occurs. This is referred to as the *isoelectric point* of the protein, and at it the particles may be supposed to be neutral in respect of the dispersion medium. The isoelectric point of gelatin is, for example, at about p_H 4.7. In more acid or alkaline media the particles would carry a positive or negative charge respectively. The protein exhibits a number of special properties at this p_H value which

marks the condition of minimum stability of the sol, when the protein is most readily flocculated. These are more particularly referred to in the section on proteins and are of great importance in brewing. Since the electrical phenomena on which they depend to a considerable extent are different in lyophobic and lyophilic systems the characteristics of these two classes of colloids must be more fully described.

(88) Lyophobic Colloids.

The *micelles*, or particles of the disperse phase in a lyophobic system, may be supposed to be surrounded by an electric double layer, consisting of the charge on the particle and an opposite charge on the dispersion medium around it. This stabilises the colloid particles, that is keeps them apart from each other, but if the electrical charge is neutralised flocculation occurs. The particles are readily precipitated by addition of a small quantity of an electrolyte, the active agent being the ion bearing a charge of opposite sign to that of the particles. The flocculating power of the added ions increases very greatly with their valency. Precipitated hydrophobic colloids cannot be dispersed again, they are said to be irreversible. Examples of the precipitation of fine particles by electrolytes are found in the deposition of silt by sea water and the precipitation of negatively charged particles, including bacteria, in water purification by positively charged colloidal hydroxide of aluminium and iron. Its connection with coagulation of proteins during wort boiling is referred to in a later chapter.

(89) Lyophilic Colloids.

The complex carbohydrates and proteins belong to the class of lyophilic colloids, which is much the more important class in brewing. Their study is rendered extremely difficult by their chemical complexity and the relatively small difference between their physical properties and those of the dispersion medium. They cannot as a rule be seen by ultramicroscopy or separated by centrifuging. Their most characteristic properties are the viscosity of their sols and the imbibition of water by the particles. They lower the surface tension of water and their sols have a tendency to foam. They are much more stable than lyophobic colloids and are not generally coagulated by small quantities of electrolytes, such as will precipitate the latter. It is usually necessary to add large quantities of salts to precipitate the proteins, the process being known as salting out. It is believed that the stabilisation of lyophilic sols in water depends not only on the electric charges on the particles but also on their hydration.

Flocculation thus depends on simultaneous discharge and dehydration, and the particles may remain dispersed at their isoelectric point, although their stability is reduced. If a hydrophilic colloid is dehydrated, it acts as if it were hydrophobic and is precipitated by electrolytes, but the original charge on the micelles may be neutralised and then replaced by an opposite charge without flocculation. The salting out of proteins by means of magnesium sulphate, etc., depends apparently on dehydration of micelles which have been neutralised by the first addition of electrolytes.

The behaviour of sulphate ions raises a point of considerable interest in brewing. The most suitable electrolytes for salting out proteins are the sulphates of ammonium, magnesium and sodium, and this depends in part on the sulphate ions. Hofmeister found that when the salting-out properties of different salts of the same metal were compared, they could be arranged in a series of diminishing effectiveness in which the anions came in the same order for different metals—fluoride, citrate, sulphate, acetate, chloride, nitrate, chlorate, iodide, thiocyanate. This was called the lyotropic series. The sulphates were found to be much more effective than the chlorides, which may even aid in dispersion. The precipitating effect of the cations decreases in the order calcium, magnesium, strontium, barium, lithium, potassium, sodium. The characteristic influence of gypseous brewing liquor on the break of wort may possibly be connected with these properties of the ions which should be taken into account, with the influence of the salts on the p_H of the wort, when an endeavour is made to explain the coagulation of the proteins. Although the electric charge is much less significant with the lyophilic than with lyophobic colloids and is only one of the two main factors in their stability, its neutralisation at the isoelectric point corresponds with a reduction in stability and generally with a minimum stability. Lyophilic colloids are generally reversible and may be redispersed after salting out, but the salts of heavy metals are much more powerful precipitants of the proteins than those mentioned above and they give irreversible precipitates.

(90) Protection.

When a very small quantity of a lyophilic sol is added to a lyophobic sol, there is a decrease in stability known as sensitisation, but if the lyophilic sol is present in excess it renders the lyophobic particles more stable to temperature changes or coagulation. This action is referred to as *protection*, and appears to be due to the formation of a sheath of the protecting colloid around the other. Gelatin, followed by isinglass, has the strongest protecting power while dextrin may also act in this way but less energetically.

Being stabilised themselves by an adsorbed layer of water, as well as by the electric charge, they confer their property of greater stability on the lyophobic particles. If the charge on the latter is opposite to that of the adsorbed gelatin or other lyophilic colloid, protection does not occur, but the system becomes very unstable through neutralisation of the charges. The use of such colloidal material as that extracted from linseed and used for preventing boiler scale is related to the phenomenon of protection, which may also occur when finings are added in excessive quantity to beer. In wort and beer the interaction of many different colloidal systems becomes very complex. Protection and precipitation may occur at the same time in different systems. Windisch used the power of sensitising other colloidal systems as a means of characterising the colloids of wort and beer, concluding that the "gum" of wort has a decisive effect on the power to form a stable foam. The action of finings offers an example of the precipitation of colloidal particles and there is another interesting case occasionally produced when two bright beers are mixed.

(91) Summary and Extension.

Throughout the malting and brewing processes there is a continual change in the colloidal state of substances originally derived from barley and hops. This is in very large part due to enzymic breakdown of such highly complex substances as starch and proteins into cleavage products, which are, in part, in a colloidal state and contribute to palate-fulness and foam-forming properties and, in part, consist of low molecular substances available for yeast nutrition. The quality of beer is probably to be more closely related to the physical condition of its constituents than to their actual chemical composition. Starch breakdown occurs mainly during mashing, when there is also a further change in the degree of dispersion of proteins and their higher cleavage products, in continuance of the changes that occurred during malting. Low temperatures favour the production of fragments of smaller size and simpler molecular composition.

In the copper, proteins in a colloidal state are denatured and coagulated, while hop constituents are extracted and dispersed as particles of colloidal character. Adsorption phenomena become of importance in the combination of malt proteins and their higher degradation products with resins and tannins from the hops. Apparently the isoelectric point of these complexes is at a lower p_H value than that of some of the proteins, so that coagulation is facilitated. During cooling there is further precipitation of colloids largely, it is believed, in the form of protein-tannin complexes.

Coagulation and precipitation of colloidal substances continues

§ 92 BIOCHEMISTRY OF MALT AND WORT

during fermentation under the influence of increasing acidity, which also reduces the solubility of hop resins. Adsorption of colloids occurs on the CO_2 bubbles, on the yeast cells and on the surfaces of the fermenting vessels, assisting in the clarification of the beer. The removal by precipitation or enzymic cleavage of colloidal substances capable of coagulation is rarely, if ever, complete, and brilliant beer usually becomes cloudy in course of time. Probably adsorption complexes of protein and tannin and others containing silica contribute to the haze formation. Even though the reactions between proteins or their higher degradation products and tannin may have attained a state of equilibrium during storage, the temperature of pasteurisation may cause a partial denaturation of their micelles and render them more prone to coagulation.

Electrolytes contributed by the brewing liquor and materials have a considerable influence on the behaviour of the colloidal constituents of wort and beer, favourably or unfavourably influencing their dispersion or precipitation, according to circumstances which are dealt with in the section on hydrogen ion concentration. The prevention of precipitation would appear to be favoured by the presence of protective colloids, such as dextrans or melanoidins of caramel and highly coloured malts.

HYDROGEN ION CONCENTRATION

(92) Ionic Dissociation.

It has already been necessary to refer to hydrogen ion concentration and use the sign p_H in connection with the properties of colloidal systems. These terms will be used so frequently in the sequel to define the reaction of wort and beer that it is necessary to explain their meaning. Biochemical reactions, whether due to micro-organisms or enzymes, are influenced to such an extent by the reaction or acidity of the liquid in which they occur that the sign p_H is almost as significant in brewing as the corresponding sign for degrees of temperature.

According to Arrhenius' theory of ionic dissociation, electrolytes, e.g., salts, acids and alkalis, are more or less completely dissociated, when dissolved in water, into two or more electrically charged constituents which are known as "ions." These ions consist of elements or groups of elements positively and negatively charged. Thus those produced by dissociation of sodium chloride are Na^+ and Cl^- , those given by calcium sulphate are Ca^{++} and SO_4^{--} . An ion may be defined as an atom or radical which has acquired a net positive or negative electrical charge equal in

magnitude to the charge of an electron or to a simple multiple of this charge. The electrical charge on the ions is indicated by the positive and negative signs or, more simply, by dots and dashes which also, by their number, indicate valency.

When placed in an electric field the ions migrate to the pole of opposite sign. An electric current passed through an electrolyte does not cause the dissociation but is conducted by already existent charged ions which, by virtue of their electric charges, travel to the pole of opposite sign on which they discharge. The negatively charged ions, discharged at the positive electrode or anode are called *anions*; the positively charged ions directed to the negative electrode or cathode are known as *cations*. In the examples of salts just given, the metals sodium and calcium yield the positive ions or cations, Na^+ and Ca^{++} , while equivalent quantities of Cl^- and SO_4^{--} form the negative ions or anions. The extent of dissociation that is the resulting concentration of ions and the quantity of, undissociated molecules in the solution, depends on the nature of the substance dissolved and on the dilution, temperature, etc. A high or low degree of dissociation is characteristic of strong or weak electrolytes respectively and complete dissociation only occurs in very dilute solutions.

The concentration of ions in a solution is expressed in terms of gram equivalents per litre or normality. The equivalent weight of an element is that which combines with 8 parts by weight of oxygen or displaces 1.008 part by weight of hydrogen. That is to say, it is its atomic weight divided by its valency. The same convention is applied to ions, valency expressing the magnitude of the ionic charge. SO_4^{--} is a divalent anion and its equivalent weight is $\frac{96}{2} = 48$. One gram per litre of hydrogen ions and 48 grams per litre of SO_4 ions thus represent the same ionic concentration.

(93) Hydrogen Ions.

According to this theory, one of the ions of every acid is the positively charged hydrogen ion, the other may be that of an element or group such as Cl' or $\text{CH}_3\text{COO}'$. Hydrochloric acid and acetic acid are examples of strong and weak acids. Though solutions of equal normality are equivalent in respect of the quantity of acid they contain and neutralise equal weights of the same alkali, they have different effects on enzymic action or the growth of micro-organisms. The terms real or active acidity are sometimes used to express this difference, of which the generally accepted explanation is found in the degree of dissociation of equivalent solutions. In some properties hydrochloric acid

§ 94 BIOCHEMISTRY OF MALT AND WORT

behaves as if it were dissociated to the extent of 91% in decinormal solution, while acetic acid of equal normality appears to be dissociated to the extent of only 1.3%, a relation which is more closely in accordance with their relative influence on micro-organisms and enzymes in biochemical reactions in dilute solutions.

Considerations of this nature have led to the special significance attached to the concentration of hydrogen ions in dilute aqueous solutions because the acidity of the solution appears to depend on it. The conception has become crystallised in the term Hydrogen ion concentration, which has proved of extreme value in all branches of biochemistry. The theory of ionic dissociation has appeared to clear up many obscurities in biological phenomena by showing that the behaviour of micro-organisms and enzymes depended, not on the total quantity of any ion present, but on the amount that is free or active.

During the last few years this theory has, however, been opposed by several physicists. One alternative suggestion is that properties which can be explained by the theory of varying degrees of dissociation are more probably due to varying degrees of activity of the ions. At greater concentrations the activity of anions and cations would be diminished by the proximity of oppositely charged ions. There is consequently a tendency to substitute the term activity for concentration of ions when solutions of strong electrolytes are in question. Further, the existence of free hydrogen ions in solutions is now very seriously questioned. If, as is believed, they are identical with the proton or unit of positive electricity they cannot exist in a free state and when given off from an acid would combine with bases or with water. This has given rise to the conception of the "hydroxonium ion" or H_3O^+ , to which the properties hitherto ascribed to the hydrogen ion may be due.

It is impossible to enter into such intricate controversies as this, but since the observed facts are related to causes which can, apparently, be related to hydrogen ion concentration, the older view of their explanation may be retained as a useful working hypothesis. Its applications described in the sequel are, however, given with all due reservation and with an open mind for future developments. The study of brewing problems has hitherto been reserved almost entirely to chemists and has hardly kept abreast of advances in physical science, from which no doubt many new ideas and interpretations of well known facts may ultimately be derived.

(94) Ionisation of Water.

Even the purest water behaves as if it were ionised to a certain

extent, giving equal quantities of H' and OH' ions. The dissociation may be represented by

$$\frac{[H'] \times [OH']}{[H_2O]} = K_w$$

in which square brackets indicate concentrations and K_w is the dissociation constant of water. Since the quantity of undissociated water may, in comparison with the extremely small proportion which undergoes ionisation, be regarded as constant it follows that the ionisation product is a constant

$$[H'] \times [OH'] = K$$

The value of the ionisation constant of water has been calculated to be 10^{-14} ,¹⁴ from which the concentrations of hydrogen and hydroxyl ions are both seen to be represented by 10^{-7} .⁰⁷ gram equivalents per litre or approximately 10^{-7} .

It is interesting to consider what this means in concrete figures. One gram molecule of any substance is stated to contain approximately 6.061×10^{23} molecules. Accordingly pure water contains $6.061 \times 10^{23} \times 10^{-7}$ hydrogen ions per litre. This equals 6.061×10^{16} or 60,610,000,000,000,000, over 60 thousand billion hydrogen ions in a litre. A litre of water is computed to contain 55.56 gram molecules or $55.56 \times 6.061 \times 10^{23}$ water molecules, so that only 1 molecule in every 555,600,000 is ionised.

(95) Hydrogen Ion Concentration. p_H .

The range of possible concentration of the hydrogen ions in different solutions is so wide and, as has been shown, is so low in water, that its expression in grams per litre is very cumbersome. Liquids such as beer or wort are supposed to contain only about one-tenthousandth to one-millionth of a gram of ionised hydrogen per litre. Changes in hydrogen ion concentration represented by much smaller fractions of a gram than these have quite a marked influence on biochemical reactions and it has been found necessary to devise a scale down to one hundred million millionth of a gram of hydrogen ions per litre, or $\frac{1}{10^{14}}$ gram. It has been calculated that a piece of paper 69,444 miles long would be required to plot the whole range of concentrations from $\frac{1}{10}$ to $\frac{1}{10^{14}}$, a quite impossible situation in view of the frequency with which it is necessary to construct graphs showing the effects of changes in hydrogen ion concentration.

This difficulty has been overcome by adoption of Sørensen's

§ 96 BIOCHEMISTRY OF MALT AND WORT

suggestion that hydrogen ion concentration should be represented by the logarithm of its reciprocal. Thus a hydrogen ion concentration of $\frac{1}{10}$ gram hydrogen ions per litre is represented by the logarithm of 10, that is by 1, while 2, being the logarithm of 100, represents a hydrogen ion concentration of $\frac{1}{100}$ gram per litre. The resulting value is expressed by p_H and if $[H']$ is the hydrogen ion concentration

$$p_H = \log \frac{1}{[H']}$$

$$\text{or } p_H = -\log [H']$$

$$\text{or hydrogen ion concentration} = 10^{-p_H}$$

(96) Acidity, Alkalinity and the p_H Scale.

Acidity and alkalinity derive a special significance when dilute solutions exhibiting the properties generally associated with these terms are studied in the light of their ionisation, on the assumption that one of the ions of every acid is the positively charged hydrogen ion and one of the ions of basic hydroxides is the negatively charged hydroxyl ion OH' .

All liquids of which water is a constituent may be supposed to contain positively charged hydrogen ions and negatively charged hydroxyl ions. The addition of an acid to water increases the apparent hydrogen ion concentration and diminishes that of the hydroxyl ions in such a way that their product remains constant, according to the equation $[H'] \times [OH'] = 10^{-14}$. Addition of an alkali brings about a similar increase of the OH' ions and decrease of the H' ions. Thus H' and OH' ions always exist together in both acid and alkaline solutions, the former being characterised by predominance of the H' ions and the latter by that of OH' ions. The hydroxyl ion concentration can always be deduced by subtracting the p_H value from 14 and both acidity and alkalinity can be expressed in terms of p_H , giving a scale on which the central point of neutrality is occupied by p_H 7. At this point the concentrations of H' and OH' are equal as they are in water. In this way acidity and alkalinity become relative terms on one single scale divided into equal unit divisions of p_H from 0 to 14.

A normal solution of an acid or alkali is defined as containing one gram equivalent of the substance per litre or one gram equivalent of H or OH as the case may be, the same basis as that on which hydrogen ion concentration is expressed. A decinormal solution of a strong acid should thus have a p_H value of 1 and a centinormal solution a p_H value of 2. Equivalent solutions of a

strong base would have p_H values of 13 and 12 respectively. Since acids and bases never appear to be completely ionised, unless the solutions are very dilute, the normality and p_H scales will not exactly coincide, but, for practical purposes, they may be considered to do so for such strong acids and bases as HCl and NaOH, as in Table 17. The actual p_H of decinormal HCl is 1.04 and of decinormal NaOH 13.07, the latter containing 0.000,000,000,000,086 or 86×10^{-14} or $10^{-13.07}$ gram of ionised hydrogen per litre.

TABLE 17.—NORMALITY AND p_H VALUES OF DILUTE SOLUTIONS OF STRONG ACIDS AND BASES

Normality of solutions	p_H values	
	HCl	NaOH
Normal	0	14
0.1 N	1	13
0.01 N	2	12
0.001 N	3	11
0.0001 N	4	10
0.00001 N	5	9
0.000001 N	6	8
Neutrality	p_H 7	

It will be seen from this table that an increase in p_H value of 1 unit actually means a tenfold decrease in the concentration of hydrogen ions, which corresponds with the definition that the scale is logarithmic with the sign altered. A p_H value of 4 represents 1,000 times more hydrogen ions than p_H 7. Though the difference in p_H values between 5.0 and 5.1 and between 5.9 and 6.0 are numerically equal, the former represents a difference in hydrogen ion concentration many times greater than the latter. The difference in hydrogen ion concentration denoted by a tenth on the scale becomes progressively greater as the p_H value diminishes from 7 to 1 by values standing in the relation of 1 to 1,000,000.

It is important to note that the central point on this scale, denoted by 7, represents neutrality or the p_H value of pure water (p_H 7.07). That the lower figures 7 to 0 indicate increasing hydrogen ion concentration or acidity up to the value corresponding with normal solutions of strong acids. Higher figures from 7 to 14 show decreasing hydrogen ion concentration or what is generally regarded as increasing alkalinity to the value representing normal solutions of completely dissociated strong alkalis. The latter solutions also contain hydrogen ions, so that the entire scale, 0 to 14, represents decreasing acidity and p_H values increase as

97 § BIOCHEMISTRY OF MALT AND WORT

acidity falls. p_H 0 represents 1 gram of ionised hydrogen per litre and p_H 14 = 0.000,000,000,000,01 gram.

Hydrochloric acid appears to be dissociated to the extent of 91% in decinormal solutions, instead of the 100% just mentioned, so that solutions of this strength would contain 0.091 gram of H⁺ ions per litre and behave as if their active acidity was measured by $\frac{9.1}{100}$ N. The apparent hydrogen ion concentration of decinormal hydrochloric acid is consequently given by this figure or by $10^{0.96} \times 10^{-2}$ (0.96 being the logarithm of 9.1), or by $10^{-1.04}$. Similarly a litre of N/10 acetic acid appears to contain 0.0013 gram of hydrogen ions and its active acidity is represented by $\frac{1.3}{1000}$ N. Its hydrogen ion concentration is therefore expressed by

$$1.3 \times 10^{-3} \text{ or } 10^{0.11} \times 10^{-3} \text{ or } 10^{-2.89}$$

and its p_H value by 2.89.

The p_H value is a more precise indication of the effect of acidity on many biochemical processes than the titratable acidity of the solutions. At greater dilutions both these acids are more fully dissociated, as shown in Table 18. The strong acid is dissociated to a greater extent than the weak and its p_H value is always lower in equivalent solutions.

TABLE 18.—DISSOCIATION OF DILUTE ACIDS

	Hydrochloric		Acetic	
	Dissociation %	p_H	Dissociation %	p_H
Decinormal acid ..	91.0	1.04	1.3	2.89
Centinormal acid ..	96.4	2.02	4.17	3.38

(97) Buffers.

Another conception which has been found to have many applications in brewing is that of buffer action. It may be simply explained by analogy with the buffers on railway trains, which minimise the effect of shocks and caused Fernbach and Hubert to apply the term *tampon* or buffer to substances which minimise the change in p_H value brought about by additions of acids or alkalis to other solutions or water. If a strong acid or alkali be added to water the p_H value is suddenly decreased or increased and very small additions will produce very considerable change of p_H in solutions containing free alkali or acid, as the case may be. On the other hand if acid be added in less than equivalent quantity

to the solution of a salt of a weak acid, the H ions it yields will unite with the anions of the salt to give molecules of the weak acid which is so slightly ionised that the p_H will be only very slightly changed. Thus the carbonates of brewing liquor exert an important buffering effect and restrict increase in the hydrogen ion concentration of wort, because H ions unite with CO_3 to produce almost unionised H_2CO_3 or, actually, H_2O and CO_2 . Similarly salts of weak bases act as buffers against OH ions, while salts of strong acids with strong bases have little or no buffering influence in either direction.

Typical buffer solutions are made by mixing 0.2N solutions of acetic acid and sodium acetate. These are characterised by definite p_H values depending on the proportions of the two constituents. The figures given in Table 19 show that the p_H increment due to each 5% of neutralisation of the acetic acid is in the order of 0.1 p_H unit.

TABLE 19—BUFFER SOLUTIONS OF ACETIC ACID AND SODIUM ACETATE

p_H value	3.72	4.05	4.27	4.45	4.63	4.80	4.99	5.25	5.37	5.57
% 0.2N acetic acid	..		90	80	70	60	50	40	30	20	15	10
% 0.2N sodium acetate			10	20	30	40	50	60	70	80	85	90

The addition of strong acid will liberate acetic acid from the sodium acetate, while alkalis would neutralise some of the free acetic acid, producing small changes in p_H of the order mentioned. The smallest change produced in this way, or the greatest buffering action, is seen to occur when half the acetic acid is neutralised. The buffer action in respect of acids would cease when all the acetate was converted to acetic acid, and to alkalis when all the acid was neutralised. Thus the buffer action of any solution is restricted to a definite range of p_H values. Buffer solutions serve as readily reproducible standards of p_H value, because this depends on the proportions of their constituents. Many suitable mixtures are available containing such substances as primary and secondary phosphates, boric acid and borates, succinic acid and succinates, etc.

(98) Buffer Titrations.

The buffer action of solutions may be determined by plotting the changes in p_H produced by successive small additions of acid or alkali. A typical graph for the titration of 50 ml. of decinormal phosphoric acid with N/10 alkali is given in Fig. 81.

The straight portion of the curve at p_H 7, when the change from

§ 99 BIOCHEMISTRY OF MALT AND WORT

KH_2PO_4 to K_2HPO_4 is half complete and additions of KOH produce only slight changes in p_{H} value, indicates a region of maximum buffering. Similar buffering actions are to be noted at about p_{H} 1.5 when H_3PO_4 is half converted to KH_2PO_4 , and at p_{H} 11 between K_2HPO_4 and K_3PO_4 . The ionisation produced when the primary or acid phosphate is formed corresponds to a p_{H} value of 5 and that for the secondary or alkaline phosphate to p_{H} 9.2. The buffer action of wort depends partly on a mixture of these phosphates derived from the malt.

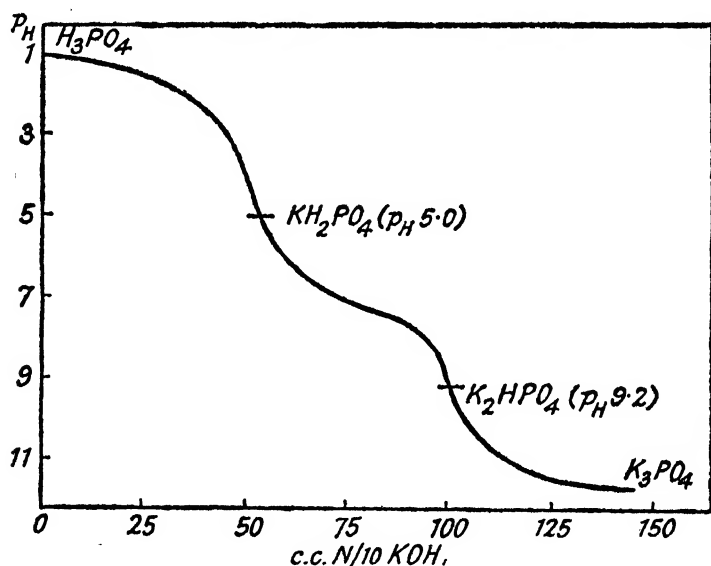


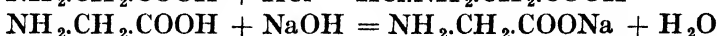
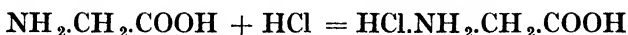
FIG. 31
TITRATION CURVE OF PHOSPHORIC ACID

The buffer action of a solution can be quantitatively defined by means of Van Slyke's buffer coefficient $\pi = d_{\text{B}}/dp_{\text{H}}$, in which d_{B} is the amount of acid added in gram-equivalents per litre and dp_{H} the resulting change in p_{H} value. The buffer coefficient π is the number of gram-equivalents of strong acid or alkali required to produce a change of one unit in the p_{H} value of the buffer solution.

(99) Ampholytes.

Substances which have the power of reacting either as an acid or base are known as amphoteric electrolytes or ampholytes. As a rule their basic or acidic functions are weak and can only be brought effectively into action by means of strong acids or bases. Aluminium hydroxide provides an example. With hydrochloric

acid it forms aluminium chloride, AlCl_3 , and with caustic soda it gives sodium aluminate, Al(ONa)_3 . Examples encountered in brewing are to be found in the proteins and protein digestion products. To take the simplest example, glycine or amino-acetic acid, which contains one NH_2 and one COOH radical, whereby it forms salts either with acids or bases, acts as a base in strong acid solutions and as an acid in strongly alkaline.



In acid solutions the dissociation is such that the glycine carries a positive charge, $\text{Cl}^- + ^+\text{NH}_3\text{CH}_2\text{COOH}$. In alkaline solutions it carries a negative charge, $\text{NH}_2\text{CH}_2\text{COO}^- + \text{Na}^+$. At some intermediate point it will give positive and negative ions in equal quantity and the total charge is at its minimum value. This is its isoelectric point when it exists as a "zwitter ion," $^+\text{H}_3\text{NCH}_2\text{COO}^-$. The isoelectric point varies with different substances and is at a lower p_{H} value when the acid character of the ampholyte predominates over the basic. "Zwitter" is German for hermaphrodite and is here used in accordance with Bjerrum's hypothesis (see Section 115).

DETERMINATION OF HYDROGEN ION CONCENTRATION

(100) Electrometric Methods.

The measurement of such an exceedingly small concentration of hydrogen ions as exists, for example, in a decinormal solution of caustic soda and is represented by 8.6×10^{-14} or a p_{H} value of 13.07 would seem almost beyond the range of possibility. The normality represents 0.000,000,000,000,086 gram per litre. In worts and beers with p_{H} values ranging between p_{H} 6 and 4 the weight of hydrogen ions would be between 0.000,001 and 0.0001 gram per litre. It is possible, however, to measure the activity of the hydrogen ions by electrical methods and to calculate their apparent concentration from the results obtained. In addition, methods based on the change of colour produced in indicator solutions at different p_{H} values have been devised.

Electrometric methods are capable of greater accuracy than colorimetric and must be used if it is desired to determine values with an accuracy of 0.01 p_{H} , but they require expensive apparatus and skilful manipulation. Colorimetric methods are much simpler and generally satisfactory for routine purposes for which an accuracy of 0.1–0.2 p_{H} is adequate. Electrometric methods, however, constitute the basis of reference against which colorimetric methods are checked and standardised.

If a metal electrode is placed in a solution of one of its salts

§ 100 BIOCHEMISTRY OF MALT AND WORT

it exerts a potential and tends to dissolve and increase the concentration of its ions in the solution but, at the same time, ions derived from the salts in solution tend to deposit on the metal until there is an equilibrium between the solution pressure and the osmotic pressure. A "hydrogen electrode," consisting of platinum coated with platinum black saturated with hydrogen, will behave in an analogous manner in solutions containing hydrogen ions and come to an equilibrium with the solution which varies with the hydrogen ion concentration of the latter. If two hydrogen electrodes are immersed in liquids with different hydrogen ion concentrations and connected by means of an inverted U-tube containing normal KCl solution, while the electrodes are connected by a wire, a difference of potential depending on the difference between the hydrogen ion concentrations, or activities, will be set up between the two electrodes. A current will then pass and can be measured by means of a suitable device in the circuit. If one of the cells contained a solution at exact normality of hydrogen ions, it could be used as a standard for measuring the hydrogen ion concentration in the other. Such a standard solution is difficult to make and, in practice, is replaced by a calomel half-cell in which a platinum electrode dips into mercurous chloride in normal potassium chloride solution. Calomel electrodes are easily prepared and maintain a constant potential over a long period. The hydrogen electrode, kept in equilibrium with an atmosphere of hydrogen by bubbling hydrogen round it, is immersed in the solution under examination. The current in the circuit connecting the two electrodes is measured in millivolts. At 18°–20° C. the E.M.F. varies as $0.058 \log [H^+]$. The observed E.M.F. is the difference between the E.M.F.'s of the two electrodes, i.e. :—

$$\begin{aligned} \text{E.M.F. observed} &= E_{\text{N-calomel}} - E_{\text{hydrogen}} \\ &= 0.283 - 0.058 \log H^+ \end{aligned}$$

$$\text{Whence } \log [H^+] = \frac{0.283 - \text{observed E.M.F.}}{0.058}$$

$\log H^+$ is negative for solutions containing less than 1 gram-equivalent of Hydrogen ions per litre, let it be represented by $-x$.

Then :—Hydrogen ion concentration $[H^+] = 10^{-x}$

and by definition x is the p_H value of the solution.

Several different methods and types of apparatus are available for determining the hydrogen ion concentration of liquids by electrometric means, but the above is sufficient to indicate the principle on which the measurement is made. The glass electrode is very useful for worts and beers.

(101) Indicators.

Indicators are substances of which the solutions vary in colour according to the reaction of the medium. Their use in hydrogen ion concentration measurements depends on the fact that the colour change occurs at a definite p_H value or, more generally, that there is a gradual change of tint over a range of p_H values which makes it possible to gauge the extent of the change at any p_H value within this range. Some indicators are compounds which form salts with either acids or bases and yield at least one coloured ion on dissociation. The degree of dissociation is in such cases altered by changes in hydrogen or hydroxyl concentration, and this causes an alteration in the colour of the indicator. This theory is not altogether satisfactory, and in many cases it is believed that the change in colour is due to a change in the constitution of the compound. Thus it is suggested that phenolphthalein in acid liquids exists in a form which can be represented to contain a lactone ring. In alkaline liquids it forms an alkali salt of another form of the compound containing a quinone group and this is red.

The change of colour over a limited transition interval of p_H values within which the two forms of the indicator exist together in varying proportions, giving a transition of colour from one form to the other, has been precisely determined for a large number of indicators of which a selection is given in Table 20. The first ten

TABLE 20.—INDICATORS

Indicator	p_H range	Colour change		gram in 100 ml.
		Acid	Alkali	
Thymol blue	1.2-2.8	red	yellow	0.04
Brom-phenol blue	3.0-4.6	yellow	violet	0.04
Brom-cresol green	3.6-5.2	yellow	blue	0.02
Methyl red	4.2-6.3	red	yellow	2.0
B.D.H. 4460	4.4-6.0	red	green	—
Brom-cresol purple	5.2-6.8	yellow	violet	0.02
Brom-thymol blue	6.0-7.6	yellow	blue	0.04
Phenol red	6.8-8.4	yellow	red	0.02
Cresol red	7.2-8.8	yellow	purple	0.02
Thymol blue	8.0-9.6	yellow	blue	0.04
Methyl orange	2.9-4.0	red	yellow	0.02
Litmus	5.0-8.0	red	blue	2.0
Neutral red	6.8-8.0	red	orange	1.0
Phenol-phthalein	8.3-10.0	colourless	red	1.0
2-4 Dinitro-phenol (α)	2.8-4.5	colourless	yellow	0.10
2-5 " " (γ)	4.0-5.4	colourless	yellow	0.10
<i>p</i> -Nitrophenol	5.0-7.0	colourless	yellow	0.50
<i>m</i> -Nitrophenol	6.8-7.4	colourless	yellow	0.50

§ 102 BIOCHEMISTRY OF MALT AND WORT

are those most commonly used for standard buffer tubes, covering a range of p_H values from 1.2 to 9.6. It will be noted that the old definition of acid and alkali, depending on the change in colour of an indicator, no longer holds. For instance, if methyl orange gives an orange colour when added to a liquid, it merely means that the liquid has a p_H value of not less than 4.0. It may still be acid.

(102) Colorimetric Determination of p_H .

The p_H value of colourless buffered liquids may be determined by adding a measured quantity of an appropriate indicator solution to 10 ml. of the liquid and comparing the colour produced with those of a series of buffer solutions of accurately known p_H values containing the same proportion of indicator. The colour of beer and wort complicates the comparison but the difficulty can be overcome in a simple manner by use of a comparator, which may be a block of wood pierced with six vertical holes to take the test tubes disposed in pairs, one behind the other. The block is pierced horizontally with cuts through which each pair of tubes can be viewed by transmitted light. 10 ml. of the beer or wort, to which indicator has been added, is placed in one of the centre holes, with a tube of water in the hole behind it. The two most closely matching standard tubes are then placed in the front row, to left and right of the test liquid, while two tubes of the beer or wort, without indicator, are placed behind them. The test tubes used are all of equal diameter, and the colour observed through any of the pairs is made up of that of the wort or beer itself, together with that produced by a given volume of the indicator. The standard buffer tubes cover the working range of the indicator with differences of 0.2 in p_H value between each pair of the series. Although the tubes are hermetically sealed, their colours gradually fade, a defect which has been overcome in the Lovibond comparator by adoption of coloured glasses standardised against B.D.H. indicators.

This method becomes increasingly difficult with darker worts or beers, but these can be diluted 10, 20 or even 40 times without great loss of accuracy in the measurement. It is sometimes difficult to get a good match with worts and beers. Colloids may adsorb the indicator to some extent and oxidising or reducing substances may affect its colour. On the other hand, the salts in the buffer solution may have an influence on the colour which may be absent in the wort. These sources of error, with the exception of the last, may be avoided by eliminating the tubes containing water and untreated wort and simply matching a mixture of the sample, indicator and buffer solution against a

mixture of similar proportions of sample, indicator and water. The salt error due to the buffer salts can be reduced by adding N/10 NaCl solution instead of water to the other mixture, as proposed in a colorimetric method described by Kolbach². Red-yellow indicators are not satisfactory for wort and beer. Those with yellow-blue virage give a much clearer colour change. Brom-cresol green is useful for beers and the B.D.H. mixed indicator 4460, covering the p_H range 4.4–6.0, is suitable for worts.

A rough determination can be made with a solution of mixed indicators, such as the B.D.H. Universal Indicator, which gives definite colour changes between p_H 3.0 and 11.0.

Colorimetric determination of the p_H value of water or very dilute solutions is complicated by the buffering action of the small quantity of indicator added. B.D.H. indicator solutions are neutralised to their half-way point and, if added to pure water, show the corresponding colour. Thus Brom-cresol green would indicate p_H 4.4–4.6, while Thymol blue might show p_H 8.6–8.8 with the same water. Water must, therefore, be treated with a reduced quantity of the indicator to minimise the effect of the reaction of the latter. The colour is then observed down the tube instead of across it and compared with buffer tubes containing a similar proportion of the indicator. It is best to confirm p_H values by a second test with another indicator, having an overlapping range.

(103) Summary and Applications.

The influence of the reaction of the medium on the course of biochemical changes brought about by enzymes, on the behaviour of colloids and on the life of micro-organisms is much more clearly comprehensible through the conception of hydrogen ion concentration or active acidity than in relation to the quantity of acid indicated by titration with alkali. The quantity of acid present in wort and beer is small but their p_H values, due to the presence of weak acids and acid salts and regulated by the existence of buffer mixtures, have important influences on the character, composition and stability of the beer. Examples are to be found in subsequent chapters in which the influence of hydrogen ion concentration on each phase of the brewing process is dealt with. There is a constant increase in acidity from wort to beer, the gradual change being appropriate to the enzymic and physical processes occurring at each stage. Abnormalities in behaviour or defects in the product result from deviations from the normal p_H value at any stage. The change in p_H values may be summarised as

§ 103 BIOCHEMISTRY OF MALT AND WORT

follows, the figures applying to English top-fermentation beers. Values higher by 0.3 to 0.5 in p_H are typical of lager brewing.

TABLE 21.—CHANGES IN p_H VALUE DURING BREWING

Stage in brewing	p_H	Influence
Mashing, distilled or carbonate liquor.	6.0-5.6	Rather high for enzymic conversion.
„ gypseous or treated liquor.	5.2-5.1	About optimum for mash tun conversion.
Boiling, hopped wort ..	5.1-5.0	Favourable for break and moderate hop extraction.
Fermentation, falling p_H ..	5.0-4.0	Favourable to yeast at first, becoming increasingly unfavourable.
Beer	4.2-3.8	Favourable to beer stability. Inimical to bacterial growth.

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CHAPTER VII

THE CARBOHYDRATES AND PROTEINS OF BARLEY AND MALT

THE CARBOHYDRATES

(104) The Biochemistry of Malting.

The chemical and physical changes in the constituents of barley brought about during malting consist, firstly, in changes in the colloidal state of such complex materials as starch, proteins, etc., followed by breakdown of the altered substances to simpler colloid and, finally, soluble crystalloid substances. The questions with which it is necessary to become familiar relate to :—

- (1) The nature of the physical and chemical changes during malting.
- (2) The agency by which they are brought about.
- (3) The extent to which they should be carried during malting.
- (4) The means for judging the extent of these changes, and
- (5) The influence of these changes and of the varying degree to which they are carried on the quality of the malt.

It would be impossible to follow these changes without some knowledge of the nature and properties of the various constituents of barley. These were referred to in a previous chapter, but little was said in respect of their chemical properties and those of their derivatives. Our knowledge of the constitution of starch, and of that particular variety of it found in barley, is so limited that it is impossible to give a complete picture of what occurs to it during malting, while similar difficulties arise in connection with the proteins and other constituents of barley. Nothing further can, therefore, be attempted here than to give such a broad, generalised account of such of their physical and chemical properties as may be useful for practical application.

Production of starch and allied compounds in plants is among the most important chemical reactions for which nature is responsible. It involves storing up the energy of sunlight which, acting through the agency of chlorophyll in the green tissues, causes carbon dioxide and water to enter into combination. The inter-

§ 105 BIOCHEMISTRY OF MALT AND WORT

mediate stages in this photosynthesis are not known with certainty, but it is widely held that formaldehyde is a primary product and that cane-sugar is formed in an upgrade, intermediate stage, leading to the production of starch. The energy fixed becomes available as the motive force of vital processes, produces heat during respiration and accounts for the rise of temperature during fermentation, all of which involve the reverse downgrade processes. Syntheses of this nature have not yet been effected artificially, but the breakdown processes can be brought about readily and lead to the production of simpler carbohydrates, known as dextrins and sugars. These are essential biochemical reactions in malting and brewing and can be studied in the downgrade sequence in which they occur.

(105) Carbohydrates.

The carbohydrates are substances which contain only carbon, hydrogen and oxygen, the hydrogen and oxygen always existing in the same proportion as in water, that is two atoms of hydrogen to one of oxygen. The two most important carbohydrates in barley are starch and cellulose. The former exists in the cells of the endosperm in the form of granules, embedded in a matrix of protein and other materials, the latter forms a considerable part of the structural elements of the grain. Although they are very different in physical properties, cellulose, for example, being much more resistant to the action of water than starch, they are both found by analysis to consist of carbon, hydrogen and oxygen in the proportions represented almost exactly by $C_6H_{10}O_5$. The slight divergence from the composition represented by this formula is due to the impossibility of freeing them completely from associated water, phosphorus, silica, etc.

The enquiry as to how these two substances, with the same percentage composition, can have such different properties raises some of the most difficult problems of organic chemistry, but it is believed to depend on the manner in which the molecules are interlocked in the colloidal physical units. The actual size of the molecules is different. In both cases it is many times greater than is represented by $C_6H_{10}O_5$. How much greater is still uncertain and the formula for both starch and cellulose is frequently written as $(C_6H_{10}O_5)_n$ to indicate this. It is at present generally agreed that Haworth's estimate of 30 as the value of n in starch satisfactorily represents its molecular unit, but this does not represent the physical unit. Many molecular units may be joined to form the physical unit as it exists in colloidal dispersions. Evidence will be given later which suggests that

this larger unit in raw starch varies greatly and may account for several hundred or more than a thousand times $C_6H_{10}O_5$.

The simplest carbohydrates or sugars have the general formula $C_n(H_2O)_n$. Compound sugars may be regarded as derived from them by combination of 2, 3 or 4 molecules, with elimination of 1, 2 or 3 molecules of water, e.g., $C_{2n}(H_2O)_{2n-1}$. The carbohydrates met with in brewing may be listed as follows, to indicate their relationships and the nomenclature of groups and individuals.

- (1) *Simple sugars*—Monosaccharides, $C_n(H_2O)_n$. $n = 3$ to 9 .
 - (a) Pentoses, $n = 5$. $C_5H_{10}O_5$, arabinose, xylose.
 - (b) Hexoses, $n = 6$. $C_6H_{12}O_6$.
 Aldohexoses—glucose, mannose, galactose.
 Ketohexoses—fructose.
- (2) *Compound sugars*.
 - (a) Disaccharides. $n = 6$. $C_{2n}(H_2O)_{2n-1}$, $C_{12}H_{22}O_{11}$.
 Reducing sugars—maltose, lactose, melibiose.
 Non-reducing sugar—sucrose (cane sugar).
 - (b) Trisaccharides. $n = 6$. $C_{3n}(H_2O)_{3n-2}$, $C_{18}H_{32}O_{16}$.
 Raffinose (non-reducing).
- (3) *Polysaccharides* in which n is very large or unknown.
 - (a) Pentosans, $(C_5H_8O_4)_n$, araban, xylan.
 - (b) Hexosans, $(C_6H_{10}O_5)_n$, starch, cellulose, glycogen, dex-
 trins, mannan, galactan,
 lichenin.
- (4) *Related compounds* containing other groups in the molecule;
 with carbohydrate groups, which may be pentosans,
 hexosans or both.
 - (a) Mived pentosans—hemicelluloses, pectins, gums.
 - (b) Inositols, isomeric with hexoses, associated with bios,
 combined with P_2O_5 in phytin.

(106) Starch.

Starch exists in plants in the form of granules, which vary considerably in their shape and size, as is shown by the photomicrographs of granules from different sources in Fig. 38. In some starches there are smaller and larger individuals and in many cases a characteristic mixture of small and large granules. Those of potato starch range between 60 and 100μ or up to $1/250$ of an inch in length, while barley starch contains large granules of about 20μ , and small ones about 4μ in diameter. The existence of structural layers around a point, known as the hilum, is clearly shown in potato starch. When starch is heated with water, the granules begin to swell at temperatures varying with their origin and finally form a gelatinous mass. The temperatures at which

§ 106 BIOCHEMISTRY OF MALT AND WORT

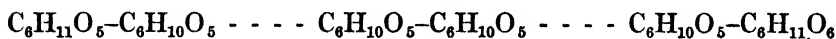
gelatinisation commences are at about 149° Fahr. for potato starch, 167° Fahr. for maize starch, 176° Fahr. for barley, rye, wheat and rice starches, and 185° Fahr. for oat starch, but, in practice, it is necessary to boil the starches to get complete gelatinisation. The granules lose their structure in this process, forming a colloidal system with water.

Starch granules are not homogeneous and two components, with distinct physical properties, can be separated from starch paste (1) by treatment with dehydrated, precipitated barley diastase, which converts one to maltose, with little action on the other,¹ (2) by Ling's method of freezing, followed by extraction with warm water, which removes one component as a colloidal dispersion and leaves the other as an insoluble residue, and (3) by Samec's² method of electrodialysis. Maquenne and Roux³ called the less resistant component Amylose. This is readily dispersed in water and completely converted to maltose by diastase. The more resistant fraction was called Amylopectin. This gives a paste with hot water and is converted mainly to dextrins by malt diastase. They held that amylopectin formed a protecting envelope to the less resistant inner portion of the granules, consisting of amylose, but the relation between the two components of starch is probably more intimate than this, the amylopectin occurring around and between amylose particles. They are alternatively known as α -amylose (amylopectin) and β -amylose (amylose), while Samec called the fraction that travelled towards the cathode in his electrodialysis process, amyloamylose and the other erythroamylose. The former, corresponding with amylose, gives a blue colour with iodine, the latter, a violet or red colour. Starch granules also contain very small quantities of phosphoric acid, silicic acid, fatty acids, lime and protein. Such figures as 0.02 and 0.17% of P_2O_5 have been found in different starches and 0.5-0.8% of fatty acids in maize and rice starch. In addition, Schryver and Thomas⁴ claimed the existence of another organic constituent, which they regarded as a hemicellulose and of which 3.8% has been reported in maize starch and 1% in rice starch.

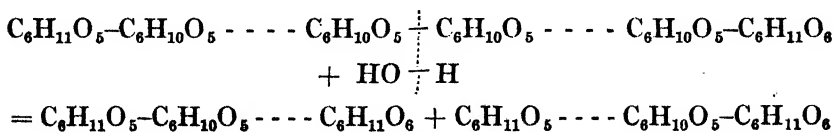
Recognition of two distinct components of starch, gave rise to theories of their conversion to different products in the mash tun, but Hirst, Plant and Wilkinson⁵ failed to find any chemical difference between amylose and amylopectin. Haworth⁶ suggests that the physical unit of amylopectin is much greater than that of amylose, differences in properties thus depending on variation in the degree of aggregation or number of chemical molecules in their physical molecules or colloidal micelles, which might influence their mash tun conversion. The difficulty of making any clear-cut separation of aggregates of this kind no doubt accounts for the

very varying yields obtained by different methods. Ling and Nanji placed the proportions of amylose and amylopectin in several starches as 2 : 1, but others have found such ratios as 1 : 4.

The problem of cellulose and its difference from starch may be left out of consideration here, since it is not altered appreciably during malting and mashing. Starch, on the other hand, is altered very much and the final result in wort, under most favourable conditions, is the production from it of a mixture containing 80 % of a fermentable sugar, maltose, and 20 % of an unfermentable dextrin. The nature of the substance or substances constituting the latter fraction is again very much in doubt and it has been realised for a long time that the best way to answer this question and to find why the products obtained in mashing vary so much under different temperature conditions in the mash tun, is to discover the constitution of the starch unit. This, according to Haworth, is represented by a chain of 24 to 30 links, each of which is a $(C_6H_{10}O_5)$ group. Richardson, Higginbotham and Farrow have, however, produced evidence that the chain constituting raw starch may consist of 1,470 links. However this may be, the molecule of starch may be represented by



The dashes indicate the indefinite length of the chain and the two end groups are here formulated rather differently from the rest to suggest the presence of a molecule of water and slight reducing properties which Richardson, Higginbotham and Farrow⁷ found were possessed by starch. This long chain can be readily broken to fragments by boiling with dilute acids, the fragments being glucose, which is $C_6H_{12}O_6$, so that starch may be regarded as a chain of glucose residues. Starch is also broken down in the mash tun, but the products are different, mainly maltose, with a smaller proportion of an unfermentable or difficultly fermentable residue of dextrans. Invariable production of the latter in enzymic conversions of starch suggests that the structure of starch is not uniform, but that its molecule contains a "knot" of more resistant material, though nothing definite can be said on this point. The following equation represents an early stage in starch breakdown :—



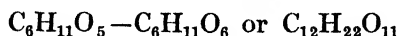
(107) Dextrins.

The above equation represents the fracture of the starch chain into two large fragments by the action of water at the place marked by vertical dots. A reaction of this kind, adding the elements of water, is known as an hydrolysis and it is thus that the breakdown of the starch molecule either by acids or by enzymes is represented. The two fragments into which the molecule is broken are here represented as two long chains of indefinite length. These are dextrins and it may be imagined that a very large number of different dextrins, with varying chain lengths and properties, might be produced by breaking the immensely long chain of starch at different points. Alternatively it may be supposed that certain links in the chain are more readily parted than others and that the number of dextrins is limited. This question still awaits an answer. Quite a number of products of this nature, for which individuality has been claimed, have been obtained by the action of enzymes on starch and have been given various names, of which malto-dextrin, α -amylodextrin, trihexosan and hexahexosan are examples. It is perhaps best to regard them all as dextrins, and to associate with them "soluble starch," which is the first product of the breakdown of the raw starch unit.

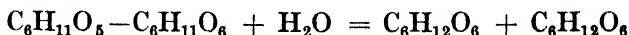
It is generally held that hydrolysis does not occur when starch is digested with 7% hydrochloric acid for 7 days at 60° Fahr. Soluble starch obtained in this way, after filtration, washing to remove acid and drying at room temperature is, according to this view, a product of physical disaggregation of the original starch unit. Richardson, Higginbotham and Farrow, however, consider that hydrolysis actually occurs and that soluble starch differs from unmodified starch, and its lower conversion products, only in chain length. They claim that it has a cupric reducing power, corresponding with varying chain lengths of from 80 to 50 glucose units. Soluble starch can be dissolved or caused to form a clear colloidal dispersion in boiling water, although the appearance of the granules differs little from that in raw starch, apart from cracks in some of them. It is the form of starch usually employed in experiments with diastase, because it is much more readily converted than raw or gelatinised starch. As such it is used as the substrate for estimation of diastatic activity. It does not reduce Fehling's solution in the processes ordinarily used in sugar analyses.

Proceeding further in the breakdown of the dextrin chains first produced, chains with a progressively smaller number of links would be obtained, all or any of which might occur in wort. Finally a point is reached when a short chain of only two links

is obtained or, alternatively, two links might be split off from the end of the starch chain, leaving at each successive stage a shorter dextrin chain. In either case this chain of two links is maltose :



Maltose in its turn can be hydrolysed by boiling with dilute acids, giving the two single links, which are glucose :



Haworth and his colleagues at Birmingham University have isolated and purified fractions from starch conversions by diastase, with chain lengths of 16-18, 10-12, 6-8 and 5-6 glucose units, as found by gravimetric assay of their methylated derivatives. They, as well as starch, all appeared to consist of continuous chains of α -pyranose units. α -amylodextrin was found⁸ to consist of 11-12 such units and different specimens of glycogen of 12-14 or 20-22 units. Cellulose differs from starch in that it consists of a chain of 200 β -pyranose units and gives cellobiose on acid hydrolysis. This disaccharide differs from maltose in that the two glucose units are united by β -linkage. These terms are defined in the next section, while fuller details of the practical implications of the investigations of the dextrans will be given in the sections on wort composition in Vol. II.

(108) Sugars.

Maltose and glucose are sugars. Both still contain a considerable number of carbon, hydrogen and oxygen atoms in their molecules and it is possible to imagine these atoms arranged in different ways in space, so that $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ and $\text{C}_6\text{H}_{12}\text{O}_6$ might both represent quite a number of different substances, with the same percentage composition but varying properties. This is actually the case—glucose and fructose (formerly called dextrose and lævulose) are both $\text{C}_6\text{H}_{12}\text{O}_6$, maltose and cane sugar are both $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.

These sugars are respectively representative of two groups of simple and compound sugars, otherwise known as monosaccharides and disaccharides. Dextrans and starch, which are composed of many simple sugars, are known as polysaccharides, as are also cellulose and glycogen. The termination *ose* is used to denote sugars, as in maltose or sucrose and saccharose, both of the latter being more scientific names for cane sugar. Glucose and fructose are both hexoses, the prefix denoting the number of carbon atoms in the molecule. There is another group of simple sugars containing 5 carbon atoms to which reference should be made as they probably occur in wort. These are the pentoses, of which

§ 108 BIOCHEMISTRY OF MALT AND WORT

xylose and arabinose are examples. The dextrins, which consist of several hexose residues, are sometimes referred to as hexosans, and the corresponding compounds, which give pentoses on hydrolysis, are pentosans.

Two important properties of the sugars, of which much more will be said in later chapters, are (1) the power of rotating the plane of a ray of polarised light either to the right or the left, known as optical rotatory power, and (2) the power of reducing cupric salts in alkaline solutions possessed by some of them. All the products of starch hydrolysis, or starch conversion, and all the sugars have optical rotatory powers and the angle through which they turn the ray of polarised light is specific for each and known as its $[\alpha]_D$. This term is defined in the sections on sugar analysis, in which great use is made of it. Evidence⁷ has been produced recently to show that starch itself and soluble starch have cupric reducing power as well as all its simpler conversion products. This property is also used in wort and sugar analysis and will be explained in due course. The sugars can be divided into those which do or do not reduce cupric salts. Of those mentioned cane sugar has no reducing properties, while maltose, glucose and fructose have this power.

Cane sugar is hydrolysed by boiling with dilute acids in a manner quite similar to the conversion of maltose to two molecules of glucose. The products of its hydrolysis are, however, glucose and fructose in equal quantities. Fructose differs from the other sugars mentioned in that it rotates the plane of polarised light to the left, glucose, maltose and cane sugar rotate it to the right. Moreover the left-handed rotation of fructose is greater than the right-handed rotation of glucose and consequently their mixture in equal quantities has a left-handed rotation. Thus, when a solution of cane sugar, which rotates to the right, is boiled with a little acid the rotation of the solution obtained will be "inverted" and the mixture of sugars obtained by concentration, equal quantities of glucose and fructose, is known as invert sugar. The equation representing the inversion of cane sugar is identical with that given for conversion of maltose to glucose, as maltose and cane sugar are isomeric and the products glucose and fructose are also isomeric, their differences being only represented by formulæ which show the varying disposition in space of the constituent elements.

This sketch of the relations between the various carbohydrates has shown the breakdown of complex to simple members of the group. This is the only way in which their relations can be shown experimentally. It has not yet been found possible to build up glucose into maltose, fructose and glucose into cane sugar

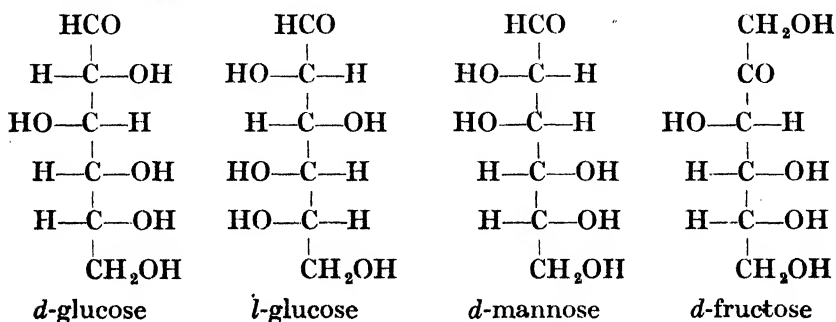
or to synthesise any of the dextrans or starch. These syntheses are, however, natural in plant metabolism. The simple sugars are produced from CO_2 and H_2O by the intervention of chlorophyll in the process of photosynthesis in green plants, and, from the simple sugars, either cane sugar or starch are synthesised as the reserve carbohydrates and cellulose as the main structural element in the plant.

(109) Constitution of the Sugars.

The properties of the sugars can be epitomised by means of constitutional formulæ based on the available experimental evidence. The following formulæ express the fact that the aldohexoses, glucose and mannose, are polyhydric alcohols and behave as aldehydes, $\text{H}-\text{C}=\text{O}$ representing the aldehyde group. Fructose, on the other hand, has many of the properties characteristic of ketones, for which reason the ketone group $-\text{CO}-$ is included in its formula. These sugars are readily oxidised to various acids and the reducing power, associated with the oxidation, enables them, like other aldehydes and ketones, to reduce silver or copper salts in alkaline solutions, such as Fehling's solution. Among the possible acids reference should be made to the special group of uronic acids, of which glucuronic acid is an example and a constituent of the molecule of hemicelluloses. These acids are formed by oxidation of the primary alcohol group $-\text{CH}_2\cdot\text{OH}$ to $-\text{CO}\cdot\text{OH}$. Another reaction, which is of value in the identification of sugars, is the production of osazones when their solutions are heated with an excess of phenyl-hydrazine in dilute acetic acid. Glucose, mannose and fructose yield the same yellow, crystalline osazone,



This substance is only slightly soluble in water and melts at 204° – 205° C. Its formation distinguishes these sugars from maltose, which gives an osazone melting between 190° and 200° C. and more soluble in water.



The striking property of optical activity possessed by the sugars, and the existence of dextro- and lævo-rotatory forms of each are also suggested by their formulæ. It has been found that all carbon compounds containing an asymmetric carbon atom, that is carbon linked with four different atoms or groups, are optically active. It is possible to show that these four atoms or groups can be arranged round the carbon atom in two different ways, which are mirror images one of the other. The two formulæ thus obtained represent two "space isomers" or stereo-isomeric compounds, explaining the existence of two substances with equal and opposite optical activities. One of these rotates the plane of polarised light to the right, the other to the left. It will be observed that the two formulæ given for glucose are mirror images and that each of the four carbon atoms to which H is joined, but not the other two, are joined to four different atoms or groups. These all contribute to the optical activity of ordinary glucose which is dextro-rotatory and is represented arbitrarily by the formula marked *d*-glucose. Its mirror image represents the lævo-rotatory form of glucose, which can be prepared by chemical means. It will further be noted that 8 sugars, isomeric with glucose, can be formulated by changing the positions of the H and OH groups around the four central C atoms. Of these, *d*-mannose is shown. Each of these can exist in dextro- and lævo- forms giving 16 isomeric aldohexoses, of which glucose, mannose and galactose occur naturally, the others have been synthesised. In a similar manner four ketohexoses, isomeric with fructose, are possible each with its dextro- and lævo- forms, giving 8 in all. It should be noted that the *d*- and *l*- nomenclature of the sugars does not indicate the direction of rotation. Ordinary glucose is dextro-rotatory and is called *d*-glucose. All the other sugars with corresponding configuration around the 5th carbon atom are called *d*-sugars. Hence ordinary fructose, which is lævo-rotatory, is described as *d*-fructose.

It is now recognised that these formulæ are inadequate to explain all the properties and reactions of glucose and fructose, for which Haworth proposed the formulæ given in Fig. 32. The molecular structure of stable glucose is there represented by a ring joining five carbon atoms and one oxygen atom, with a primary alcohol group as a side chain. The carbon atoms are numbered to indicate their position in the ring and the bonds are printed thick and thin to suggest a solid molecule. The carbon atom marked with an asterisk is referred to as that of the potentially aldehydic group and production of the aldehydic form of glucose by opening the ring is shown in the fourth formula. Glucose also sometimes reacts as if it existed in an unstable form, known as γ -glucose. This is represented by a ring of four carbon

atoms and one oxygen atom, with a longer side chain. These two forms of ring are named after pyran and furan, of which they are respectively characteristic, and the two forms of glucose are often conveniently referred to as glucopyranose and glucofuranose. Similar ring structures are ascribed to fructose, but this sugar appears to be much more prone to react as if it existed in the unstable γ or furanose form than is glucose. This is shown in the third formula in Fig. 32.

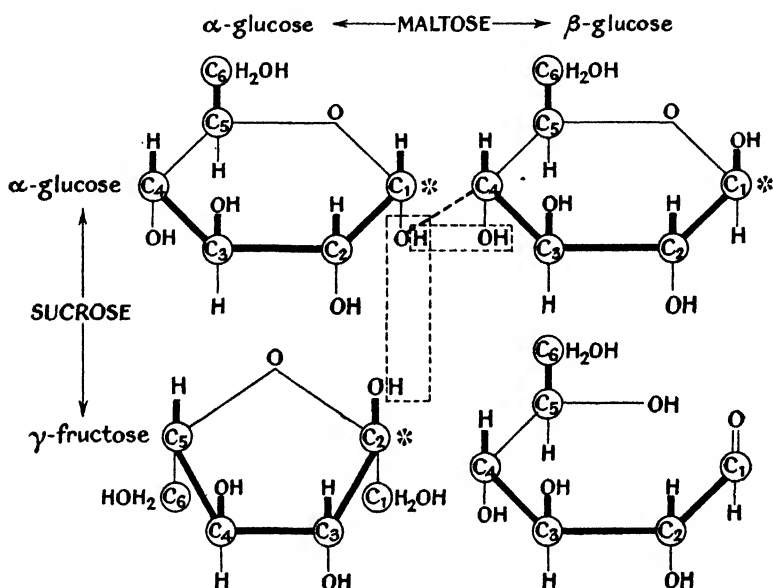


FIG. 32

FORMULAE OF α - AND β -GLUCOSE AND γ -FRUCTOSE, SHOWING FORMATION OF MALTOSE AND SUCROSE

It will be noted that the ring formula for glucose introduces a fifth asymmetric carbon atom, that marked C_1 . Transposition of the H and OH around this carbon atom provides an explanation of the very interesting property of muta-rotation shown by many sugars. By muta-rotation is understood the change in rotation exhibited by a freshly prepared cold water solution of the sugar when it is allowed to stand. The change can be brought about by boiling the solution for a few moments or very rapidly by addition of a few drops of ammonia. It is explained by the existence of two forms of the sugar which readily change one into the other. These two forms have different optical activities but their relative quantities are rapidly brought to the same equilibrium when the solution of either is boiled. The $[\alpha]_D$ is then that accepted as the specific optical rotatory power of the sugar in question. The practical application of this is dealt with in Section 246. The

§ 109 BIOCHEMISTRY OF MALT AND WORT

optical activities of the two forms of the more important sugars and of the solution when equilibrium is reached are given in Table 94. The form which rotates the plane of polarised light more to the right, or has the greater positive angle, is known as the α -form and the other as the β -form. In this way the two formulæ for α - and β -glucose, given in Fig. 32, are derived. The angle of glucose falls on boiling, that of maltose rises, while a solution of cane sugar shows no muta-rotation, for a reason which will be now explained.

Fig. 32 also shows how the hexoses may be supposed to combine to form disaccharides and affords an explanation of some of the properties of the latter. These may be divided into two groups of reducing and non-reducing sugars, typified by maltose and cane sugar respectively. It has been stated that maltose gives two molecules of glucose on hydrolysis. Its own molecule is consequently held to consist of two glucose molecules united through oxygen, after removal of H from one of them and OH from the other, as indicated by the dotted lines in the diagram. One of these glucoses is α - and the other β -glucose and it will be observed that the potentially aldehydic group of the α -glucose is destroyed in the process of condensation, but that of the β -glucose is unchanged. The existence of this unchanged group explains the reducing power of maltose, which is less than that of the two glucoses together, weight for weight. Since one of the groups marked with an asterisk remains, maltose shows muta-rotation. Cane sugar, which gives glucose and fructose on hydrolysis, is represented by condensation of these two sugars in a similar manner but, in this case, the potentially reducing groups of both hexoses are destroyed, cane sugar having no reducing power or muta-rotation.

Other disaccharides are represented in a similar manner and their structure resembles that of an important group of natural products, known as glycosides, which consist of glucose or another hexose united with a non-sugar group. It is therefore possible to regard the disaccharides as glycosides and denote them correspondingly according to the two hexoses which they give on hydrolysis, and also the position of the carbon atom, generally C₄ or C₆, through which the second hexose is attached to the C₁ of the other through oxygen. Thus the disaccharides of interest in brewing are as follows, sucrose only containing a hexose in the furanose form.

- Maltose β -glucose—4— α -glucoside.
- Lactose, α -glucose—4— β -galactoside.
- Melibiose, β -glucose—6— α -galactoside.
- Cellobiose, β -glucose—4— β -glucoside.
- Sucrose, α -glucopyranose—fructofuranose.

It is generally held that the disaccharides must be hydrolysed to their constituent hexoses before fermentation, although some evidence for the direct fermentation of maltose has been obtained. Their fermentation is consequently only effected by yeasts which contain an enzyme capable of causing the hydrolysis. Thus brewery yeasts ferment maltose and cane sugar because they contain the enzymes maltase and sucrase (invertase), but they contain no enzyme capable of breaking the particular bond in lactose and cannot ferment it. Lactose is, however, fermented by certain other yeasts. Melibiose is particularly interesting in that it is fermented by bottom but not by top yeasts, which can be distinguished by fermentation experiments with this sugar. Raffinose, the only trisaccharide that need be mentioned, is constituted by glucose, galactose and fructose, which is equivalent to a combination of melibiose and fructose. Top-fermentation yeasts can only break the bond between melibiose and fructose and ferment the latter, while bottom yeasts hydrolyse raffinose to its three constituents and ferment them all. It is for a similar reason that the cellulose of barley is not broken down during germination or mashing. The enzymes which convert starch cannot hydrolyse it to its constituent cellobiose groups, but it is broken down and fermented by some bacteria.

The constitutional formulæ described have been constructed to show the relations between the various atoms and groups in the molecules, as these have been revealed by experiment. They should therefore provide a summary of the reactions and properties of the sugars and be very helpful to students, but they must not be regarded as the final word on the molecular structure of the substances they represent. It has frequently been found impossible to account for newly discovered reactions on the basis of accepted formulæ and these have been modified as knowledge increased, in the manner exemplified by development of Haworth's formulæ from those of Emil Fischer. Moreover a certain freedom of movement must be conceded to the elements in sugar molecules. Thus a solution of glucose may be supposed to contain the mutarotating modifications, the aldehyde form and, perhaps, others, which cannot be represented by one formula. The practical value of these intricate studies will become clearer by consideration in later sections of the use made of them in the endeavours to discover the nature of wort constituents.

(110) Pentosans and Pentoses.

The pentose sugars do not occur in nature, but exist in the form of condensation products, similar to the dextrans or hexosans. These are widely distributed in plants and are known as pentosans,

§ 111 BIOCHEMISTRY OF MALT AND WORT

of which xylan and araban form part of the structural elements of barley, included in the hemicelluloses. This word is unfortunate, since it implies a close relation to cellulose, which does not appear to be justified. Hawley and Norman⁹ have divided the hemicelluloses into two groups. One, more closely associated with cellulose, they have called cellulosans and shown to be generally xylans. The other and larger group they refer to as polyuronides. These give hexoses, pentoses and uronic acids on hydrolysis, including glucose, mannose, xylose and arabinose. Some of these substances are broken down to soluble pentosans by cytase during germination and, perhaps, in the mash tun, but others are unattacked and remain in the grains, from which Preece¹⁰ separated uronoxylans and uronoaraban. The structure of the pentosans and pentoses is similar to that of the hexosans and hexoses, but they possess the characteristic property of giving furfuraldehyde, when distilled with dilute hydrochloric acid, a reaction used for their quantitative estimation. The pentoses differ from the hexoses in being unfermentable by brewery yeast.

The pectins, to which frequent reference will be found in recent brewing literature, consist of calcium and magnesium salts of complicated carbohydrate associations, in which galactose, galacturonic acid and arabinose exist. They would thus be included in the second group of hemicelluloses. Their partial hydrolysis, with liberation of calcium and magnesium in inorganic form, may possibly be an essential feature of modification during malting. Irish moss, made from certain sea-weeds, contains rather similar substances, such as lichenin, frequently referred to as mucilages. The gums are allied to these but more soluble in water. All these substances give viscous colloidal sols with water and yield pentoses and hexoses on hydrolysis.

PROTEINS

(111) The Proteins of Barley and Malt.

Proteins are substances containing nitrogen as well as carbon hydrogen and oxygen, and in some cases sulphur as well. They are the final stable nitrogen compounds formed in plants and animals and are even more complex in their constitution than starch. Like the latter they may be visualised as consisting of an immense number of units, but the chains in which these units are combined are in some cases branched and in others include rings. Moreover the units are not all the same, so that a protein may be likened to a building constructed of a large number of different coloured bricks, including many of each colour.

No protein has yet been analysed with sufficient exactness to determine the nature of all of its constituent bricks, but several have been sufficiently well examined to establish their main architectural features and identify many of their parts. The proteins are classified by their solubility in different reagents. Thus the proteins of barley were distinguished as :—

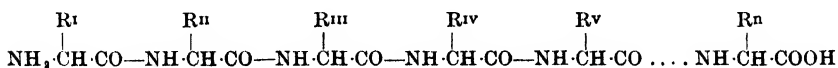
- (1) Water-soluble protein or Albumin.
- (2) Salt-soluble protein or Globulin, soluble in 5% K_2SO_4 solution.
- (3) Alcohol-soluble protein or Hordein, soluble in 70% alcohol.
- (4) Insoluble protein or Glutelin. Not dissolved by any of the above reagents, but soluble in dilute caustic soda solution.

These are typical of four groups of plant proteins which need not be further described here, but it may be noted that characteristic proteins occur in different plants. Their elementary composition is very varied, the nitrogen content ranging between 15 and 19%. Analyses of hordein and of a protein fraction separated from malt by Osborne and Campbell are given in Table 22.

TABLE 22.—COMPOSITION OF PROTEINS

	Hordein	Malt Protein
Carbon	54.3	53.2
Hydrogen	6.8	6.7
Oxygen	20.9	23.2
Nitrogen	17.2	15.7
Sulphur	0.8	1.2

Such analyses give little idea of the nature of proteins, the constitution of which may be represented in a very general and diagrammatic form by the formula

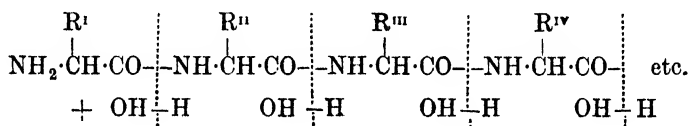


It is not implied that this formula is a complete representation of the building plan of a protein or that the elements shown in it are always joined together in the way indicated, but it does serve to explain many of the results obtained when the molecule is broken down by hydrolysis, either by an inorganic reagent or an enzyme. The most striking thing about it is that the molecule

§ 112 BIOCHEMISTRY OF MALT AND WORT

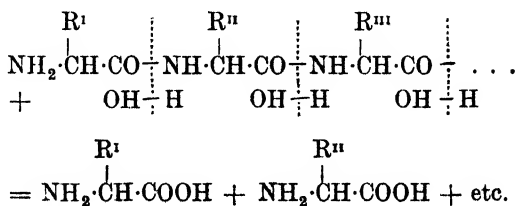
is represented by a number of groups of similar type, but differing from each other by attachment of a side group or chain, which may be H or CH₃ or some other much more complicated group of radicals. These are represented by R^I, R^{II}, etc., to indicate that they may be very varied, and exceedingly numerous. The size of the molecules of proteins is even more doubtful than that of starch, but according to Svedberg's deductions from ultracentrifuge studies and Adavi's from osmotic pressure measurements, the molecular weight of crystalline egg albumin is about 35,000 and that of plant globulins of the order of 200,000.

The proteins of barley may be imagined as built on the plan indicated and their behaviour during malting and brewing may be visualised by carrying the simile further and imagining a building constructed from a large number of different coloured bricks. The mortar holding these bricks together, indicated in the formula by the dashes -- is the "peptide linkage," ·CO—NH·. In some proteins there may be as many as 30 different coloured bricks and probably several of each. The constitution of the protein can be ascertained by demolishing the whole building and examining the separated bricks. The following formula represents this demolition by means of hydrolysis.



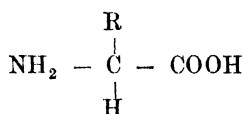
(112) Hydrolysis of Proteins.

The hydrolysis of proteins can be effected by boiling with 20% hydrochloric acid or with caustic soda solution and, if carried to the limit, the resulting breakdown or degradation products prove to be amino-acids, as represented in the next equation. These may consequently be regarded as the individual bricks of the protein edifice.



Amino-acids are organic acids containing both NH₂ and COOH, the amino and carboxyl groups, by virtue of which they exhibit both basic and acidic properties. Glycine may be given as an

example of a simple amino-acid. It is $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, and is derived from acetic acid, $\text{CH}_3 \cdot \text{COOH}$ by replacement of one of the hydrogen atoms of the methyl group by NH_2 . Leucine or β -iso-propyl- α -amino-propionic acid is a somewhat more complex amino-acid represented by $(\text{CH}_3)_2 : \text{CH} \cdot \text{CH}_2 \cdot \text{CH} (\text{NH}_2) \text{COOH}$. However simple or complicated these mono-basic amino-acids may be, they can be represented by the general formula :—



Reference will occasionally be made to another group of compounds, which also contain the NH_2 group, but must not be confused with the amino-acids. These are the amides, formed by replacement of the OH of the carboxyl group of organic acids by NH_2 . Thus acetamide is derived from acetic acid and is represented by $\text{CH}_3 \cdot \text{CO} \cdot \text{NH}_2$. Asparagine is an important compound in plant metabolism and yeast nutrition. It contains both an amino and amide group and is represented by the following formula :—



The analyses of hordein in Table 23 are partial representations of the constitution of a typical protein. That they are so incom-

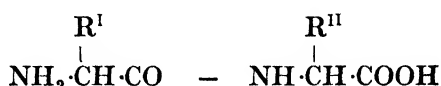
TABLE 23.—ANALYSES OF HORDEIN

Amino-acids	Osborne and Clapp (1907)	Kleinschmidt (1907)
Glycocoll	0.00	0.00
Alanine	0.43	1.34
Valine	0.13	1.40
Leucine	5.67	7.00
Proline	13.73	5.88
Phenylalanine	5.03	5.48
Aspartic acid	—	1.32
Glutamic acid	43.20	41.32
Serine	—	0.10
Cystine	doubtful	—
Tyrosine	1.67	4.00
Oxyproline	doubtful	—
Arginine	2.16	3.14
Histidine	1.28	0.51
Lysine	0.00	0.00
Ammonia	4.87	4.34
Total	78.17	75.83

plete is some indication of the great difficulties encountered in protein investigations. They show the large number of different amino-acids which constitute a protein.

(113) Products of Protein Breakdown.

The hydrolysis of proteins resembles that of starch in that it takes place in stages, successively yielding products of greater simplicity, containing fewer amino-acids. The nature of these products may be best realised by consideration of substances containing only two amino-acids, analogous to maltose in starch breakdown. These substances are known as dipeptides and may be represented by :—



A tripeptide is formed by the union of a dipeptide to another amino-acid by means of a second peptide linkage and, in a similar manner, tetrapeptides and polypeptides are produced by addition of another or a number of amino-acids. This condensation may continue right up to proteins and may be supposed to represent the manner in which the latter are synthesised in plant metabolism. Such syntheses can be effected artificially but no one has yet succeeded in carrying them as far as proteins. A number of di-, tri- and tetra-peptides with a few more complex still have been obtained in this way from amino-acids and are consequently well known as individual crystalline compounds. The more complex products are by no means so well known. So far they can only be recognised as groups of substances with analogous properties. These groups, given in order of decreasing complexity, as they would be encountered in protein degradation are :—

Meta-proteins. Produced by very gentle hydrolysis of proteins. Still retain many of the properties of the protein from which they were derived.

Proteoses (formerly known as albumoses). These still retain some of the properties of proteins. They may be defined as partial hydrolytic products of proteins which are soluble in water, not coagulated by heat but precipitated by saturating their solutions with ammonium sulphate or zinc sulphate. This is known as “salting out.”

Peptones. These represent a further stage in protein breakdown and they are not precipitated by saturating their solutions with the above salts.

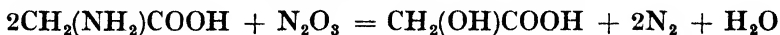
Polypeptides and Amino-acids. Simpler compounds of known constitution as already described.

The polypeptide, peptone and proteose groups grade one into another and the methods of separation by precipitation do not separate compounds of very distinct properties. Several reagents are capable of dividing a mixture of protein degradation products into reproducible fractions, but all such separations are empirical and indefinite. Some of the methods employed will be described in later sections in connection with the analysis of wort. Among the precipitants used are tannin, phosphotungstic and phosphomolybdic acid.

The formulæ given above for the proteins and their breakdown products show that these all contain at least one NH_2 or amino-group and one COOH or carboxyl group, at opposite ends of their molecules. It will also be observed that the proportion of free amino-nitrogen in the molecule increases from the proteins down to the amino-acids. In the proteins the percentage of NH_2 is very small, on account of the size of the molecule and the immense preponderance of other groups in it. In the simplest polypeptides and amino-acids the proportion of NH_2 is relatively large. It is possible to measure the COOH and NH_2 end groups and, consequently, the complexity of a protein degradation product can be assessed by the percentage of either found. Analyses of this kind were used in the Guinness Researches and the various products were distinguished by the percentage of their nitrogen existing in amino-groups, which was called the "Amino Index." This method suggests a possible means for differentiating and defining the various groups of protein degradation products by their amino-nitrogen content. Thus 10 to 20% of the nitrogen of proteoses may belong to amino-groups, while 20 to 30% of the nitrogen of peptones might exist in that form.

(114) Reactions of the Amino-group.

Two reactions are largely used for measurement of the amino-group in wort analysis. That between an aliphatic amino-group and nitrous acid is represented by the equation

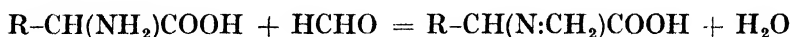


The quantity of nitrogen evolved thus measures that present in the amino-group, the apparatus now generally used for this analysis being that of Van Slyke, described in 1911.

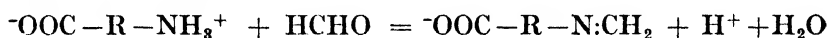
Another method very frequently used for determining amino-nitrogen is that devised by Sørensen and generally known as "formol titration." It applies more particularly to the nitrogen in mono-amino-acids, which do not redden litmus or taste acid in solution, because the acidity of their COOH group is masked by the basicity of the NH_2 group. When formalin is added to

§ 114 BIOCHEMISTRY OF MALT AND WORT

their solutions, the amino-group is changed in such a way that its basicity is suppressed, after which the COOH can be titrated with N/10 NaOH against phenol-phthalein and, since the COOH and NH₂ existed in the amino-acid in equivalent quantities, the amino-nitrogen can be calculated from the COOH found. The reaction with formaldehyde or formol can be represented by an equation showing the production of a methylene compound from the amino-acid.



An alternative formula indicating the existence of zwitter ions in an amino-acid is



This method of analysis is not of universal application and the use of the term "amino-nitrogen" for the nitrogen determined may lead to misapprehension, for which reason the term "formol-nitrogen" is to be preferred. Thus in a diamino-acid, containing two NH₂ or amino-groups with one COOH group, only half the amino-nitrogen would be calculated from the result of the titration. In addition it does not distinguish between amino-acids and polypeptides or the amino-nitrogen contained in proteins or any of their higher degradation products. One free amino-group is shown in the general formulæ given for proteins and polypeptides, and this would be measured by the analysis. Although a proportion of the formol-nitrogen found in a wort analysis, for example, would be derived from proteins and their higher degradation products, the proportion of their nitrogen combined in a form which is subject to the formol titration is very small. Much the greater quantity would be derived from amino-acids and the lowest polypeptides, in which amino-nitrogen forms a relatively high proportion of the total nitrogen. The formol titration is consequently widely used to obtain an indication of the extent of proteolysis in wort, the nitrogen so found being ascribed without serious error to the simplest products of protein breakdown.

The nitrogen contained in the peptide group can be estimated by determining the increase in amino-nitrogen produced by hydrolysis by fairly concentrated acid. This is shown in the following equation. The reaction appears simple, but in practice it is difficult to find a method of hydrolysis by which accurate results for "peptide-nitrogen" can be obtained in such a complex mixture as wort.



(115) Physical Properties of Proteins.

Certain of the physical properties of proteins and of their higher degradation products are of considerable importance in their influence on the behaviour of wort and beer. They are characterised by exhibiting the properties of amphoteric electrolytes (see Section 99), and by some definite isoelectric point. This has been determined for several proteins and found, for example, at p_H 4.6 for gelatin and at about 5.5 for serum globulin. Many of the properties of proteins have been found to be exhibited in lowest degree at their isoelectric point, and, in consequence, some of the effects of these properties are at a maximum.

PROPERTIES OF PROTEINS AT THEIR ISOELECTRIC POINT

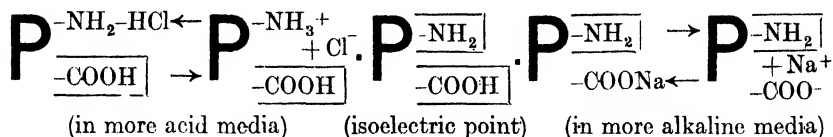
- (1) Solubility in water is at a minimum and hence
 - (a) turbidity is at a maximum,
 - (b) precipitation by alcohol is at a maximum.
- (2) Viscosity is at a minimum.
- (3) Lowering of the surface tension of water is at a minimum, hence foam formation, in so far as it depends on this, is at a minimum.
- (4) Swelling of the protein in water is at a minimum.
- (5) Osmotic pressure is at a minimum.
- (6) Coagulation is at a maximum.
- (7) The power of protecting lyophobic colloids is at a minimum.

The protein degradation products existing in wort and beer are also amphoteric substances and their isoelectric points are very significant in regard to their behaviour and to the properties of beer. These isoelectric points do not coincide but probably spread over a fairly wide range of p_H values. Many of them may be close to that of gelatin and around p_H values of 4.6–4.8, but other degradation products remaining in wort after boiling probably have isoelectric points at between p_H 5.0 and 5.5 or approaching that of serum globulin.

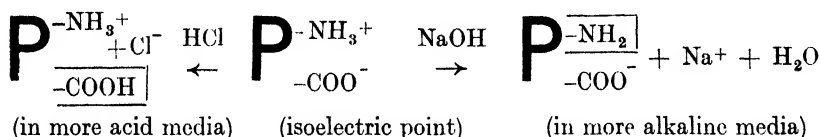
The behaviour of proteins in brewing can, to some extent, be visualised from formulæ indicating their electrical charges in media of varying hydrogen ion concentration. The main mass of the protein molecule is represented by P, to which are linked the NH_2 and $COOH$ groups that give it its amphoteric character. The protein is regarded as neutral at the isoelectric point, but this may be explained in two ways. According to Loeb, the neutrality is due to suppression of ionisation, the protein having a tendency to act as a weak base or acid, as the reaction becomes more acid or alkaline on either side of the isoelectric point. It would then combine with acids or bases, as the case may be, and tend to be

§ 116 BIOCHEMISTRY OF MALT AND WORT

ionised as shown in the first equation. Square brackets represent the unionised part of the molecule.



According to Bjerrum's "Zwitterion" hypothesis, ionisation is, on the other hand, held to be at its maximum at the isoelectric point. The molecule would, however, still be neutral at this point, because it is supposed to be equally ionised as an acid and as a base. At p_H values above or below the isoelectric point, one type of ionisation is considered to be suppressed. The behaviour of the protein with an acid or base would thus be represented by :



Whichever of these hypotheses may give the better explanation of the behaviour of proteins at their isoelectric points and of their electrically neutral state, the result is that the particles carry a stronger positive charge as the medium becomes more acid and *vice versa* with additions of alkali. As the positive or negative charge increased, the ions carrying charges of the same sign would continually repel each other more strongly, with the result that the protein would become more dispersed and the physical properties of the system, be it wort or beer, would alter in ways that will be dealt with in later sections.

(116) Coagulation of Proteins.

A completely satisfactory explanation of the flocculation of proteins by boiling their sols is lacking, but it would appear to take place in two stages. The first of these is probably chemical in its nature, involving dehydration of the protein particles or some change in the manner of their association with water. This stage is known as *denaturation*. Aggregation of the protein particles follows and results in coagulation. This is impeded if the p_H value of the liquid is removed from the isoelectric point of the protein. Thus dilute solutions of egg albumin cannot be coagulated by boiling unless their p_H is near 4.6-4.8, but the properties of the liquid are altered and the boiled sol behaves more like a lyophobic than a lyophilic system, which it was originally, and flocculation is brought about by small salt additions.

There is also a definite difference in the optical properties of the original and denatured sols. The former shows a Tyndall effect, but this is much increased in the latter, in which discrete particles can be detected by dark-ground illumination in the microscope, by which the field of the original sol would be evenly illuminated. These differences suggest an increase in size of the particles, due to agglutination, and also an increased difference between their refractive index and that of water, due to dehydration. A similar course of events, probably involving gradual changes in properties of the proteins, may explain the varying behaviour of wort in the copper. The break must be more or less unsatisfactory according as the denaturation and subsequent aggregation of denatured particles is incomplete. The readiness with which these changes take place varies with different substances and is materially influenced by the p_H of the medium. The composition of malt and the resulting wort are subject to considerable variation, explaining differences in break, while the conditions are also complicated by the presence of salts. Coagulation in proteins is also believed to be related to disulphide groups in their molecule.

If any of the original proteins of barley remain unaltered in wort, a point which has not yet been determined, they would be water-soluble albumins and salt-soluble globulins. The former are coagulated by heat, but probably not so readily or completely as egg albumin. Globulins resist coagulation, and are only completely precipitated at their isoelectric points, which are comparatively high. Consequently they might be found in boiled wort. The effect of the p_H value of the medium on coagulation may be illustrated by its effects on dilute solutions of egg albumin. These will remain clear for several months if kept at 2° C., but if the temperature is raised, precipitation in a 1% solution at p_H 4.8 will take place at 60° C. At p_H 4.4 the coagulation temperature becomes 80° C., and at a p_H value of 4.25 or lower it is incomplete even at 95° C., only an opalescence being observed. Similar but not such marked influences may effect coagulation in the copper, where the natural p_H is probably higher than the isoelectric point of the coagulable proteins present and a reduction towards that point is generally desirable. If the egg albumin is in concentrated solution when heated, the entire mass will set to a gel, but in dilute solutions the albumin separates as flocks, such as those which form in the copper. Forms of energy other than heat will cause coagulation of proteins. Thus it may occur at the interface between an egg albumin solution and air under the influence of surface energy. High pressure and irradiation with ultraviolet light will also bring it about.

The various proteins existing in wort have different isoelectric

§ 117 BIOCHEMISTRY OF MALT AND WORT

points, but the effect of salts is to widen the zone over which coagulation can occur and thus facilitate coagulation of the greatest number of proteins, and coagulation which does not occur in complete absence of salts. Coagulation is least in wort at about p_H 7 and also does not occur when the p_H is reduced below 3.7, while a p_H value of 4.6 is very favourable. Electrolytes or mineral salts in solution assist discharge of the proteins, but the activity of the various ions differs. The divalent cations of calcium and magnesium discharge negatively-charged proteins much more actively than monovalent sodium ions. Similarly divalent anions, such as SO_4^{--} , discharge positive micelles more actively than monovalent Cl' ions. It is thus probable that gypsum functions in this way in the copper, explaining the well-known beneficial effects of gypseous waters.

It is rather generally held by brewers that redispersion of coagulated proteins may occur if boiling is too long continued in the copper, thus giving wort and beer from which protein may be precipitated as the p_H changes during fermentation or storage. Satisfactory evidence for the reversal of denatured proteins does not, however, appear to have been produced, and the determination of nitrogen in boiled worts also indicates that re-solution does not occur but that the coagulation increases with boiling time. Heating at the isoelectric point results in very rapid denaturation, but this does not occur when albumin is heated in acid solution. If such a heated solution is brought to the isoelectric point and then rapidly cooled, flocks are precipitated consisting of a shell or skin of denatured protein surrounding a core of undenatured albumin. If the solution is kept hot for a short time after bringing to the isoelectric point, the whole of the protein is denatured and gives a gummy coagulum. Since coagulation is most complete between p_H 4.6 and 5.0 and the p_H of wort may vary considerably from these figures, an explanation of the generally assumed redispersion may be found in this.

(117) Determination of the Nitrogen in Wort.

In view of the extreme difficulty encountered in the identification of any of the numerous nitrogenous substances existing in wort and the rather indefinite results so far attained by methods of fractional precipitation or salting out, the separations made use of in analyses of extracts of malt and worts are usually restricted to the nitrogenous substances coagulated by boiling. These are generally regarded as albumin. The analysis consists in determining (a) the total nitrogen content of the wort, (b) the

nitrogen in the boiled and filtered wort, the difference giving (c) the nitrogen in the coagulum. The Kjeldahl method is used for the nitrogen determinations.

The results give the nitrogen in three forms : (a) Total nitrogen, (b) permanently soluble nitrogen or non-coagulable nitrogen, and (c) coagulable nitrogen. The formol-nitrogen is also sometimes determined. Simple analyses of this kind are capable of giving a good deal of information on the composition of malt or wort, but it will be recognised that they do not estimate the quantity of any particular nitrogen compound or definite group of compounds. The results are consequently expressed as percentages of nitrogen found in one or other of the forms specified.

The same convention is used in expression of the results of analyses depending on separation of fractions of the nitrogenous substances by addition of reagents or salting out. Thus fractions precipitated by tannin or phospho-tungstic acid are estimated as nitrogen and expressed as tannin-N or phospho-tungstic-N. In a similar manner such terms as Protein-N, Peptide-N, Amide-N, etc., are used in more ambitious analyses in which an endeavour is made to estimate the quantity of nitrogen in these different forms.

Although it is impossible to give the actual quantity of nitrogenous substances in which the nitrogen determined by the Kjeldahl process in the simple fractionations existed, it is sometimes desirable to obtain an approximate estimation of it. The convention has consequently grown up of multiplying the percentage of nitrogen found by 6.25 under the assumption that the average nitrogen content of proteins is 16%. The results would then be given as total protein, permanently soluble protein, etc. The percentage of nitrogen in proteins varies so considerably that this factor is not at all accurate and certainly should not be used for fractions, such as the permanently soluble, which consist mainly, if not entirely of protein degradation products. It is probable also that a factor of 6 would be more accurate for the proteins of barley and malt.

(118) Summary.

The most important reserve carbohydrate of barley is starch, which is believed to be constituted by condensation of a large, but uncertain and probably variable, number of glucose molecules. The constitutional formula of starch is consequently given as a chain of glucose residues. On hydrolysis starch is broken down ultimately to its constituent glucose molecules, through stages consisting of dextrans and maltose. Very little is known

§ 118 BIOCHEMISTRY OF MALT AND WORT

of the individual substances included in the group of dextrans, but they are believed to be constituted similarly to starch by combination of a number of glucose residues, the difference from starch consisting in their shorter chain lengths. The penultimate stage in starch hydrolysis, or the last stage in its conversion in the mash tun, is the compound reducing sugar maltose, in which two glucose residues are combined. Cane sugar is a disaccharide of the same percentage composition, but it has no cupric reducing power and on hydrolysis gives equal proportions of glucose and fructose, the mixture being known as invert sugar. The hemicelluloses, which exist in the structural elements of barley, resemble starch in that they give glucose by acid hydrolysis, but differ from it in that they contain pentose sugars as well as the hexose glucose in their molecules. The polysaccharides, starch and hemicellulose, have highly colloidal characters and the simplification in structure produced by hydrolysis is accompanied by gradual reduction in these properties until the crystalloidal sugars are obtained.

The importance of the proteins and protein degradation products in brewing depends mainly on certain general properties which they exhibit in colloidal dispersions and on the gradually diminishing degree in which these properties are exhibited by their degradation products. The latter become increasingly diffusible through membranes and hence more readily available as sources of nitrogen for yeast nutrition as they are simplified to a greater degree. The more complex protein derivatives, proteoses and peptones, are largely instrumental in contributing to the palatibility of beer, foam formation and head retention. The amino-acids are the principal yeast nutrients. The great complexity of the molecules, not only of the proteins themselves but also of their higher degradation products, has made it impossible, up to the present, to make much progress in the identification of individual substances in wort and beer or to elucidate their properties by chemical methods. Advance in knowledge of their significance in brewing may be more confidently expected from study of their physical chemistry.

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CHAPTER VIII

ENZYMES

GENERAL PROPERTIES OF ENZYMES

(119) The Nature of Enzymes.

In 1830 Dubrunfaut discovered that an extract of malt had the power of converting starch into sugar, which at that time was not distinguished from glucose, and in 1833 Payen and Persoz precipitated an active substance by adding alcohol to the extract. They attributed the starch conversion to the presence of a ferment to which they gave the name of diastase, the first example of the now very extensive list of naturally occurring agents of digestion, respiration, fermentation and other metabolic processes in plants and animals. The process of starch conversion appeared to be of a similar nature to that of fermentation and when Pasteur proved that the latter was due to living organisms a distinction was drawn between "organised ferments" and "soluble or unorganised ferments." This naturally caused some confusion and in 1878 Kühne suggested that the latter should be called "enzymes." The word signified "in yeast" and indicated the belief that there was something of the same nature in yeast to cause the fermentation of sugar. It was, however, not till 1897 that E. Buchner proved that yeast did actually contain an enzyme or enzymes capable of fermenting sugar and laid the foundation of the modern study of ferments.

Enzymes are generally supposed to be individual chemical entities, but none has yet been prepared in a pure state. Active preparations can, however, be obtained from the living tissues containing them by methods of adsorption, precipitation or dialysis. These preparations contain a high percentage of nitrogen and show characteristics of proteins but these tend to become less marked with purification. Highly crystalline, but still colloidal preparations of certain enzymes, urease, pepsin, trypsin, and carboxy-polypeptidase, have been prepared and retain protein character. In general, however, the existence of enzymes is only demonstrated by their activities. They remain intangible and very elusive to ordinary methods of chemical investigation.

Willstätter's conception of their nature has gained wide

acceptance and affords a unifying explanation of otherwise apparently unconnected properties. According to his hypothesis a colloid carrier or protector and an active group are required to constitute an enzyme system. The colloid carrier, which is generally a protein, is not necessarily any particular substance but the active group is specific, though it may be attached to many proteins and some of its properties may be altered according to the nature of the carrier, to the behaviour of which many of the properties of the enzyme can be related. The assumption of an intermediate compound between enzyme and substrate, or substance acted upon, provides a working hypothesis, in which connection Emil Fischer's analogy of the fit of a lock and key may be taken as according with their marked specificity. By this is meant the fact that an enzyme can only act on some particular substrate or, more generally, on some group of allied substances.

(120) Enzymes as Catalysts.

The action of diastase on starch, or of enzymes in general on other substrates, closely resembles that of very active catalysts. They promote changes in organic matter which can only be effected with considerable difficulty by ordinary chemical means, by such strong reagents as mineral acids and at comparatively high temperatures. Thus enzymes act so energetically in the conversion of starch or inversion of cane sugar that the change takes place at the ordinary temperature in living organisms, while considerable heat is required with acids or inorganic catalysts. The reverse reaction or synthesis of starch and cane sugar, typical of plant growth, cannot be brought about by chemical means. It must not be supposed that the mechanism of enzyme action is the same as that of inorganic catalysts, from which they differ in the limited range of substances on which each can act. The similarity is, however, so great that enzymes may be regarded as active biochemical catalysts and have been defined as catalysts of definite organic nature with specific activities, formed in living cells but acting independently of the cells.

(121) Soluble and Insoluble Enzymes.

The last part of the definition implies that enzymes can retain their activity when removed from the cells in which they normally exist. In certain cases enzymic changes are brought about in solutions by introduction of undamaged cells or organisms in which they occur, by secretions from tissues under conditions which appear to preclude entry of the substrate into the cells or by extracts of tissues from which all cell fragments have been removed. The changes produced in germinating barley would

appear to be produced by secreted enzymes which are referred to as "extra-cellular." In other cases it is necessary for the substrate to diffuse into the cells containing the enzymes, which are then referred to as "endo-cellular." Maltase and zymase are examples of the latter group. No sharp differentiation of enzymes in this way is possible and it is becoming more usual to distinguish those which are freely excreted by living cells or can be obtained in solution by direct extraction or after autolysis as "lyo-enzymes" and those which exist in the insoluble state or can only be liberated by destruction of the cells as "desmo-enzymes." The quantity of soluble enzyme that can be obtained by extraction depends very much on previous treatment of the tissues in which it existed or on the conditions of extraction. Thus the diastase and proteolytic enzymes of malt would generally be regarded as soluble but they cannot be completely extracted from ground malt by cold water.

(122) Enzyme Activity.

Since enzymes cannot be characterised as individual substances or their quantity determined by any ordinary method of analysis, and the only evidence of their existence is that afforded by decomposition of substances in natural biological fluids or extracts to which no reagent has been added, special methods are necessary to measure their activity. These generally depend on determination of the quantity of some product of the enzyme action under specified conditions or on the progress of some visible change in the substrate. The quantity of water involved in enzymic hydrolyses is very small in comparison with the total quantity of water present in the solutions in which the reactions take place. The latter may consequently be considered as unimolecular reactions. The rate of change in many enzymic reactions, however, deviates considerably from the law of mass action as applied to these. Brown and Glendinning¹ found that the rate of change during the hydrolysis of starch by diastase does not conform to the logarithmic law. In a 3% solution of soluble starch, the amount of transformation was found to be very nearly a linear function of the time until 30 or 40% of the starch had been hydrolysed, after which the rate was approximately logarithmic.

In such cases as this, comparative measurements of the activity of enzyme solutions can be based on determination of the quantity of product formed in a given time under strictly standardised conditions. Thus the Lintner method for determining diastatic activity stipulates that the quantity of starch converted should not exceed 45% of the amount originally present to comply with the Law of Proportionality enunciated by Kjeldahl in 1879.

(123) Effect of External Conditions on Enzyme Activity.

The activity of enzymes is materially influenced by the conditions under which they operate. In particular it is increased or diminished by changes in (1) temperature, (2) reaction, that is the acidity or alkalinity of the medium, and in (3) concentration of substrate or quantity of water present.

Enzymic changes, like ordinary chemical reactions, are activated by increase in temperature but much more rapidly than the latter. On the other hand enzymes are comparatively easily destroyed by heat. Every enzymic change may consequently be regarded as a balanced reaction, the balance being between activation and enzyme destruction. The two together, activation and destruction, result in increase of activity with rising temperature up to an optimum, followed by decrease until the enzyme is destroyed. The curve representing this has a gradual rather than a sharp inflexion and the optimum temperature varies with other existing conditions. In laboratory experiments it is usually found between 100° and 130° Fahr. for different enzymes, and the temperature or zone of temperature found for any particular enzyme in this way is frequently referred to as its optimum temperature. This will not usually agree with that at which it shows the greatest activity in practice under very different conditions. Thus the optimum for starch conversion in the mash tun is much higher than that found *in vitro* with more dilute solutions. The optimum temperature, as measured by the extent of change in the substrate, must also vary with the time allowed for the reaction, on account of the opposing factors of activation and destruction. If the time is measured in days the optimum would be much lower than if it were in hours, while it would be much higher if minutes only are allowed. This point has important applications in the mash tun.

The impossibility of attributing any optimum for temperature or other external factor, unless all other conditions under which it was determined are stated, must be emphasised. Thus the optimum temperature varies with the p_H value of the medium, concentration of the enzyme and substrate, presence of salts, proteins, etc., and the duration of the experiment. The temperature at which enzyme activity is destroyed also varies widely with other conditions. It is usual to consider the temperatures at which it is reduced by one-half or destroyed in one hour at the optimum p_H value as distinctive characters. For malt diastase these are usually placed at 131° and 140° Fahr.

Under otherwise specified conditions, each enzyme reacts most actively at a specified hydrogen ion concentration in the

§ 123 BIOCHEMISTRY OF MALT AND WORT

medium. The p_H optimum varies rather widely with different enzymes and with the same enzyme when other conditions, such as temperature, concentration or time of reaction are varied. Figures by Hopkins, Cope and Green² are given in Table 24 to show this. These give the percentage of maltose produced in 30 minutes at 37° C. (98·6° Fahr.) and 58° C. (136·4° Fahr.) from 100 ml. of 2% soluble starch solution containing 1·739 gr. of dry starch at various p_H values by 1 ml. of a solution of precipitated barley diastase. The velocity constant K at 37° C. is calculated from

$$K = \frac{1}{t} \cdot \log_e \left(\frac{a}{a-x} \right)$$

assuming that $a = 65·6$, t being measured in hours.

TABLE 24.—INFLUENCE OF p_H ON SACCHARIFICATION OF SOLUBLE STARCH BY BARLEY DIASTASE

p_H	Per cent. Maltose produced		Velocity constant K at 37° C.
	At 37° C.	At 58° C.	
3·7	27·65	2·60	0·475
4·2	46·90	14·24	1·087
4·67	47·50	19·30	1·115
5·4	44·60	18·87	0·989
6·2	42·35	12·85	0·900
7·1	42·15	9·25	0·892
7·8	35·10	0·86	0·679
8·2	27·90	0·30	0·481

In these experiments the optimum p_H appeared to be at 4·76 at both 37° and 58° C., but the form of the curve differed in that the fall due to more rapid destruction at higher p_H values was accentuated at the higher temperature. It will be noted that the enzyme activity was much greater at the lower temperature. The optimum p_H found corresponds very closely with that adopted in the Institute of Brewing standard method for determination of the diastatic activity of malt, but in the mash tun at a temperature of 150° and with a much greater substrate concentration, maltose production is greatest at a p_H value of about 5·1. Saccharification is possible over a range of hydrogen ion concentration represented by p_H 2·2 to 8·5.

The relative abundance of water is an extremely important factor in governing the direction and final point of equilibrium attained in enzymic reactions and with time, temperature and hydrogen ion concentration, it is among the most significant factors conditioning enzymic changes in malting and brewing.

A good example is found in the optimum and varying resistance of malt diastase to heat in presence of different proportions of water. It is rapidly inactivated above 140° Fahr. in the dilute solutions used in laboratory experiments, when its optimum is between 100° and 130° Fahr. With the greatly reduced proportion of water in the mash tun, the optimum is raised to 140° Fahr. and the enzyme will withstand temperatures of 160° to 170° for some time. On the malt kiln, with the moisture of the substrate reduced to 2%, the enzyme will resist temperatures as high as 212° Fahr. for a considerable time without destruction.

Many of the most important enzyme reactions are concerned with the breakdown of substances in a colloidal state and depend on the condition of the substrate. This is of importance in the mash tun conversion of starch, though probably complicated by the existence of more than one constituent of diastase with distinct activities. The starch of raw grain is not converted unless it is previously gelatinised and the hard ends of under-modified malt are similarly resistant. Two aspects of enzymic conversion must consequently be considered together, suitable preparation of the substrate as well as appropriate conditions for activation of the enzyme.

(124) Activating and Inhibiting Substances.

In certain cases it is known that enzymes cannot function except in the presence of another substance or "activator" naturally produced in the same tissues as the enzyme. This is referred to as a co-enzyme or kinase. Thus the group of enzymes responsible for fermentation was separated by Harden and Young³ by ultrafiltration from an inactive thermo-stable "cozymase" in the absence of which the enzyme could not ferment sugar. Reference is also made in Section 137 to the activation of one of the constituents of malt diastase, believed to exist in an inactive state in barley, by liberation of amylo-kinase during germination.

The term "complement" has been used for activating substances obtained from outside sources and not associated with the enzyme in nature. These may extend the action of enzymes to the breakdown of substances which they do not normally attack. Pringsheim separated such a complement from yeast autolysates and attributed conversion of the 20% of stable dextrin normally produced in starch conversions to presence of an accessory substance of this kind. A striking case of activation is presented by papain, which normally only acts on proteins, but in the presence of small quantities of hydrocyanic acid is enabled to attack peptones.

Enzyme activity is, on the other hand, inhibited by certain substances, for example, by the salts of some heavy metals, strong acids or alkalis and by fluorides. The restricting action of bright copper beakers on diastatic action may cause trouble in analyses. The extended action of enzymes is also frequently inhibited by accumulation of products of the reaction, but these do not destroy the enzyme.

(125) Nomenclature of Enzymes.

As the present knowledge of enzymes largely depends on their activities, they are classified according to the nature of the changes which they bring about. Thus there are groups comprising amylolytic, proteolytic and lipolytic enzymes which break down starch, proteins and fats respectively. It has been pointed out that such terms as amyloclastic and proteoclastic more correctly describe their activities and they are consequently used by some authors in place of the former. A nomenclature derived from the nature of the reaction brought about or from the name of the substrate acted on with the termination "ase" is now generally adopted. Thus there are Hydrolases, Oxidases, Desmolases, Amylase and Maltase.

The hydrolases bring about hydrolysis and by this means break down complex molecules into simpler substances with addition of the elements of water. For convenience the hydrolases may be divided in three groups, examples of all of these being found in brewing.

1. Enzymes which hydrolyse esters, e.g., *Lipases* which convert fats into glycerol and fatty acids. *Phosphatases* which liberate phosphoric acid from organic combinations.

2. Enzymes which hydrolyse carbohydrates, e.g., *Amylase*, *sucrase* (or *invertase*) and *maltase* which act on starch, cane sugar and maltose respectively.

3. Enzymes which hydrolyse nitrogen compounds. These include the important group of proteolytic enzymes, of which *Proteinases* and *Peptidases* are examples, and *desamidases* which liberate ammonia or amines from organic combinations, e.g., *Asparaginase* which hydrolyses asparagine, yielding aspartic acid and ammonia.

Enzymes which catalyse oxidations are known as *Oxidases*, and those which bring about transformations without additions of water or oxygen are *Desmolases*. The last group includes all enzymes which bring about true rupture of molecules, the name being derived from two Greek words meaning "bond-breakers." Among them are certain fermentation enzymes included in the group of enzymes comprised in the term *Zymase* which convert glucose into ethyl alcohol and carbon dioxide and *Decarboxylase*

which liberates carbon dioxide from certain keto-acids. Included in the same group are enzymes involved in oxidation-reduction reactions and referred to as *Oxido-reductases*, as enzymic reductions do not occur unaccompanied by oxidations. *Catalase* and *Peroxidase* stand rather apart from these as activators of hydrogen peroxide in oxidation reactions. Certain names which came into common use before this nomenclature was introduced are still retained. Thus *Diastase* signifying the "separation" of the two constituents of starch then believed to exist, was suggested by Payen and Persoz to designate the first enzyme recognised and is still used for the group of starch-converting enzymes, while rennin, pepsin, trypsin, erepsin, papain and bromelin are used for definite protein-digesting enzymes and *zymase*, named after yeast, in which it exists, is a convenient designation for the sugar-fermenting enzymes.

THE ENZYMES OF BARLEY AND MALT

(126) Function of the Enzymes.

One of the main objects of enzymic action in plants is to change colloidal and insoluble reserve food material into simple soluble substances which can diffuse through the cell walls and be utilised inside the cells in some way by the organism. Thus the changes produced in the starch of barley during germination consist in progressive simplification of a highly complex, non-diffusible, colloid substance, probably through several stages represented by soluble starch, one or more dextrins and maltose to simple hexose sugars which are soluble in water and capable of diffusion through the cell membrane. A large proportion of the simplified material is subsequently re-synthesised to substances of similar nature to those from which it was originally derived and so build up the structure of the growing plant. These syntheses are provisionally regarded as due to the activity of the enzyme concerned in the original breakdown.

Advantage is taken of the varied properties of enzymes to utilise the activities of those present in malt to the best advantage in brewing. This does not mean that conditions in the mash tun must be so adjusted that their activities can be exerted to the fullest extent, indeed the temperatures commonly employed in the infusion mash are considerably higher than the optimum of any of the enzymes present. It is generally desirable to restrict the conversion of starch to some extent in order that the wort may contain an adequate quantity of dextrins, rather than the maximum amount of maltose. This makes possible a certain

§ 127 BIOCHEMISTRY OF MALT AND WORT

flexibility in mashing and gives the brewer power to increase or decrease the proportion of fermentable sugar in the wort.

The circumstances are rather different with the enzymes which break down the proteins of malt. Their temperature optima are lower than those of starch-converting enzymes and they are greatly restricted in activity at ordinary mashing temperatures. They also appear to be more sensitive to hydrogen ion concentration, the p_H of a normal mash being rather higher than the optimum for their activity. It is frequently desirable to activate them, and this is done either by mashing at about 100° Fahr. or by raising the hydrogen ion concentration of the mash, or reducing its p_H value, by methods which are described in a later chapter. Further control over enzyme action is made possible by boiling part of the mash in decoction processes. This renders the substrate more readily attackable when the boiled part of the mash is returned to the bulk in which active enzymes still exist. The high temperatures reached in later stages of mashing tend to accelerate certain enzymic changes, but at the same time rapidly destroy the enzymes. Nevertheless the increased activation over a very short period is utilised in some circumstances, more particularly with the liquefying function of diastase.

(127) Diastase.

Simple experiments reveal a striking difference in the behaviour of cold water extracts of barley and malt with starch paste. While the latter rapidly liquefy and saccharify gelatinised starch at temperatures between 100° and 140° Fahr., extracts of barley have very little action and only liquefy the starch extremely slowly. That this is not due to absence of enzymes in barley extracts can be shown by allowing them to act on soluble starch, which is saccharified almost as readily by barley as by malt extracts. The enzyme cannot, however, be satisfactorily extracted from barley unless the latter is very finely ground and even then the saccharifying activity can be very much increased by extraction in presence of a proteolytic enzyme, such as papain. A further difference between the diastases of barley and malt is found in the extent to which they will saccharify soluble starch at temperatures under 130° Fahr. Malt diastase yields about 80% of maltose, the other products being dextrans of ill-defined composition. Barley diastase, on the other hand, only converts 60–65% of the starch into maltose *in vitro*, the remainder being converted into a dextrin, to which its discoverer, Baker,⁴ gave the name of α -amylodextrin. This substance, like starch, produces a blue colour with iodine however prolonged the conversion may be, but it is not formed from starch by malt diastase. It is insoluble

in alcohol of 80% strength and over and can be separated quantitatively from maltose by pouring the conversion liquid into strong alcohol. The maltose can be crystallised from the alcoholic solution much more readily than from a malt conversion liquid.

The power to liquefy starch paste becomes apparent in malt on about the third day of germination and increases during the actively growing period. Experience in the brewery would seem to suggest that liquefaction is an essential preliminary to mash tun conversion, and, further, that the liquefying function of diastase is considerably more resistant to destruction by heat than the saccharifying. It is well known that starch in under-modified malt resists conversion at the ordinary mashing temperature, but is brought into solution during sparging with water at a higher temperature. It is then sometimes not completely saccharified, a mishap which is attributed to destruction of the saccharifying function of the diastase by the high temperature reached in the mash tun. Optimum conditions for the exercise of saccharifying and liquefying activities are set out in Table 25.

TABLE 25.—DIASTASE OF BARLEY AND MALT

Enzyme activities	Action on soluble starch		In mash		Maltose produced % of starch
	Opt. temp. Fahr.	Opt. p_H	Opt. temp. Fahr.	Opt. p_H	
Barley, saccharifying..	104°–122°	4.5–4.7	—	—	60–65
Malt, saccharifying ..	113°–131°	4.65–4.85	140°–148°	5.1	80–82
„ liquefying ..	152°–158°	4.0–5.0	158°–170°	5.5	—

Observations of this kind suggest that the diastase of malt has two distinct functions of liquefaction and saccharification, and that barley diastase is practically devoid of the former. The simplest deduction is that barley contains an enzyme capable of saccharifying soluble starch and that a second enzyme with the power to liquefy gelatinised starch is developed during malting. Although the two functions of malt diastase appear to be so distinct, it should not be assumed that malt diastase necessarily consists of two enzymes, a liquefying and saccharifying diastase, and that barley diastase is identical with the latter. There is, for example, a possible alternative explanation in the production during malting of some substance which activates the barley enzyme and enables it to liquefy gelatinised starch. This view was, however, shaken by separation of two enzymes from malt diastase and identification of barley diastase with one of them. Various theories have been proposed to account for the differences between barley and malt diastase and agreement has not yet been reached

§ 128 BIOCHEMISTRY OF MALT AND WORT

between their contending advocates. These are described in Section 137. They are the result of attempts to solve a very complex and interesting scientific problem, but may seem at present to have little concern in practical brewing.

It is sufficient for the present purpose to accept the view that malt diastase is a complex of several enzymes, of which the most important are referred to as α - and β -amylase. It may be provisionally accepted that barley contains β -amylase partly in an active state and partly dormant and that the α -amylase also exists in it in an insoluble, combined or inactive form. It is generally believed that no starch-converting enzymes are produced during malting. Activation of dormant β -amylase may be attributed to the action of proteolytic enzymes on its colloidal protein-like carrier, and that of the dormant α -amylase to development of an activator, known as amylokinase. α - and β -amylase thus take the place of liquefying and saccharifying diastase respectively, but they are held by advocates of this theory to act conjointly on starch and not successively as was formerly believed.

Certain diastatic enzymes obtained commercially from bacteria may be referred to here as they have possible applications in brewing. The activity of "superclastase," for example, is essentially liquefying. The optimum temperature for liquefaction exhibited by these enzymes is very high, about 176° – 180° , and the activity is not destroyed in starch liquids until about 212° Fahr. The optimum reaction is also much more alkaline than that of malt diastase, being at about p_H 6.8–7.0, and liquefaction is not prevented until p_H 8.5. They produce about 30% of apparent maltose from starch, the dextrins give a yellow colour and are unfermentable but readily saccharified by malt.

(128) Cytase.

Less is known of the enzymes that break down pentosans and higher polysaccharides other than starch. That which attacks the hemicellulose of the endosperm during germination is known as cytase, a name which probably covers a group of enzymes capable of hydrolysing mannan and pentosans. It may still exist in kilned malts in which xylanase activity was measured by Lüers and Malsch.⁵ The activity was found to increase rapidly during germination, finally attaining a value 2.5 times that of the original barley enzyme, but it fell very rapidly towards the end of kilning until it was lower than in the barley. Its optimal activity was found to be at 104° – 113° Fahr. and p_H 5, being destroyed in $\frac{1}{2}$ hour at 140° Fahr. It may assist in the mash tun conversion of hemicelluloses, if not destroyed on the kiln, as it is able to

saccharify the insoluble pentosans of malt husks and spent grains as well as such soluble pentosans as xylan (Baker and Hulton⁶).

(129) Maltase.

Although the conversion of starch by diastase may be considered as completed when its molecular simplification has been brought down to that of maltose, there remains the possibility that maltose should be further converted to glucose :



This completion of the series of reactions is ascribed to an enzyme, maltase, which differs from diastase in that it operates inside the cells and is not extracted from them by simply macerating unbroken cells in water. Its optimum activity is placed at 95°–104° Fahr., and at a p_{H} value between 4.5 and 5.0. It is weakened or rapidly destroyed in laboratory experiments at 122° Fahr. This enzyme occurs in barley and is probably of importance in its metabolism. It is also found in pale dried malts and the formation of glucose in wort and, in considerable quantity, in commercial malt extracts made from lightly kilned malts may be ascribed to its activity, though other explanations have been advanced. The existence of maltase in malts kilned at much higher temperatures than 122° depends on increased resistance in absence of water, but its activity is very considerably reduced at higher kiln temperatures and may be destroyed.

(130) Invertase.

The existence of invert sugar and cane sugar in malt suggests the presence of an enzyme capable of hydrolysing cane sugar or of synthesising cane sugar from glucose and fructose. This is sucrase or invertase, which acts on cane sugar in a manner which can be formulated in the same way as the hydrolysis of maltose, except that one molecule each of glucose and fructose, which together constitute invert sugar, are produced instead of two molecules of glucose. The optimum conditions for the action of invertase in laboratory experiments are p_{H} 4–5 and 131° Fahr.

(131) Proteolytic Enzymes or Proteases.

The proteolytic enzymes are analogous to the starch-splitting enzymes in that they operate by activating hydrolysis and thereby break down the protein molecules into progressively simpler compounds. The process of rendering the proteins soluble and non-coagulable may be compared with the liquefaction of starch

§ 128 BIOCHEMISTRY OF MALT AND WORT

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§ 131 BIOCHEMISTRY OF MALT AND WORT

paste. The subsequent hydrolysis through peptones and polypeptides to dipeptides corresponds to the conversion of soluble starch through dextrans to maltose. The final scission of a dipeptide to amino-acids resembles the splitting of maltose to two molecules of glucose by maltase; the enzyme responsible for this last reaction also appears to be an endo-cellular enzyme, like maltase.

The proteolytic enzymes are divided into two large groups, proteinases and peptidases, according as they reduce proteins and proteoses to polypeptides or attack the latter. The former are subdivided into pepsinases, tryptases and papainases, distinguished by different ways of attacking the protein molecule. The peptidases have similarly been divided into carboxy- and amino-polypeptidases, dipeptidases, and amino-peptidases according to the structure of the peptides which they attack. In nature they occur in mixtures and it is only by recent advances in methods of separating enzymes that it has been made possible to study their individual activities. This differentiation should be borne in mind in connection with the use of enzyme preparations for stabilising beers by degradation of proteins. Those containing animal pepsin or vegetable papain are essentially proteinases, and break down proteins to derivatives of medium molecular complexity. Others are capable of activating a more profound degradation by inclusion of peptidases. The main groups of proteinases are also distinguished by their ability to function most actively in acid, neutral or alkaline media, Pepsinases operating at p_{H} 2 on positively charged proteins, Papainases at p_{H} 4-7 on particles near the isoelectric point, Tryptases at p_{H} 8-9 on negative protein ions. The animal proteinases are of the pepsin and trypsin types. Those of barley, formerly called proteases, are of the papain type of vegetable proteinases. The peptidase group includes polypeptidases and dipeptidases.

The malt proteins in cold water extracts preserved aseptically undergo a relatively slow but thorough degradation at 95°-108° F., while at 122° the action is more rapid, but the degradation is superficial. It is not yet known whether the degradation to peptones and dipeptides is due to one or more enzymes. Provisionally it may be ascribed to one proteinase with an optimum activity at p_{H} 4.6-5.0, the isoelectric zone of many proteins. (Hopkins and Burns.⁷) Green malt has been found to contain at least two dipeptidases to which optima at p_{H} 7.8 and 8.6 have been ascribed. (Sato.⁸) They were believed to be capable of acting only on the simplest polypeptides or dipeptides of wort and were distinguished as dipeptidase 1 and 2 according to their splitting action on alanine-glycine, glycyl-glycine and leucyl-glycine.

Dipeptidase 1 was active only in respect of the first and last of these dipeptides, to which dipeptidase 2 was only slightly active.

Waldschmidt-Leitz and Purr⁹ found that the proteolytic enzymes of malt appear suddenly when the rootlets are approaching 1 cm. in length and before the amylase is activated, an observation which suggests that the activity of the latter is dependent on preliminary proteolysis. Germination at comparatively low temperatures favours the production of proteolytic enzymes during malting. The sensitiveness of the peptidases to heat would make it appear improbable that they should still exist in kilned malt or take part in mash tun conversion at 140°–150° F. Their action would apparently be mainly or entirely confined to the period of germination. This does not necessarily preclude the formation of amino-acids during mashing, since these may result in the course of protein digestion by other enzymes.

It is almost impossible to summarise the temperature optima for the proteolytic enzymes of malt, but those given in Table 26 represent the results of recent investigations. Only one proteinase is included following the view that only one enzyme is responsible for the production of soluble nitrogen, permanently soluble nitrogen and formol-nitrogen in mashing, although others hold that two are necessary to explain the results obtained. The temperature optima depend on the conditions, being about 10° Fahr. higher in the mash than under laboratory conditions. The p_H optimum of proteinase is near the isoelectric point of the substrate and becomes more alkaline the higher the temperature.

TABLE 26.—PROTEOLYTIC ENZYMES OF GREEN MALT

	Temperature optimum	p_H optimum
Proteinase, <i>in vitro</i>	122°	4.3
„ in mashing	130°–140° F.	4.6–5.0
Dipeptidase 1, <i>in vitro</i>	95°–104° F.	7.8
Dipeptidase 2, „	95°–104° F.	8.6

Estimation of the activities of proteolytic enzymes is carried out by measuring the extent of their action on such substrates as crystallised egg albumin, gelatin, edestin or suitable dipeptides, but values obtained in this way are difficult to apply in practice to the different substrates existing in barley or in wort. A second uncertainty in the estimation of proteolytic activity arises from the difficulty of measuring the fission products. The changes are generally followed by estimation of the reduction in quantity

§ 132 BIOCHEMISTRY OF MALT AND WORT

of coagulable nitrogen or increase in permanently soluble nitrogen and formol-nitrogen in the reaction solutions. Degradation of proteins results in an increase of the total soluble nitrogen, which includes coagulable nitrogen and permanently soluble nitrogen. Subsequent processes may be marked by decrease in the proportion of coagulable nitrogen and a corresponding increase in the permanently soluble nitrogen. The increase in formol-nitrogen gives an approximation to the activity of the peptidase when conditions permit of its action, though it must be noted that increase in the polypeptides and dipeptides produced by proteinase also involves an increase in formol-nitrogen, which does not exist entirely in the form of amino-acids.

Some suggestions as to the development of proteolytic activity during malting may be drawn from investigations on sprouting wheat by Mounfield.¹⁰ Little increase in the proteolytic activity was found to occur during the first two days, but rapid development of activity occurred during the next four days until it reached 10 times its original value on the 7th day. Some doubt exists about the lag phase of two days since the absence of increase in proteolytic activity may be due to incomplete diffusion of enzymes into water at that stage. The extraction is greatly facilitated as germination proceeds, a fact which is also obvious in determinations of diastatic activity in barley and malt.

Storage of wheat in absence of light is accompanied by steady loss of the power to develop proteinase activity on germination, the loss amounting to about 67% in two years. A similar state of affairs may result during the storage of barley.

Stimulation of enzymic activity by traces of cyanides is a common property with plant proteinases or papainases. Both the proteinase and dipeptidase of sprouted wheat are stimulated in this way. 0.001 N cyanide produces the greatest effect with the former, increasing its activity by 60% and at the same time shifting the optimum p_H value from 4.1 to 4.8. Most peptidases are inhibited by cyanide, but that of wheat was found to be activated to a small extent, with a simultaneous shift of the optimum p_H value with leucyl-glycine from 7.3 to 7.8, and with glycyl-glycine from p_H 7.9 to 8.1.

(132) Isolation of Enzymes by Adsorption.

Proteolytic enzymes provide an example of modern methods of isolating individual enzymes by adsorption on suitable substances and subsequent separation from the adsorbent by elution. Basic adsorbents are supposed to concentrate at their surfaces acid substances which exist in the solutions to which they are added. Aluminium hydroxide is an example of these. Acid

adsorbents, such as kaolin, adsorb bases. Alumina should thus adsorb enzymes if they are of an acid nature, together with other acid substances. It was found by Lüers and Malsch¹¹ and by Hopkins¹² that alumina adsorbs proteinase and peptidase from green malt extracts under suitable p_H conditions, at p_H 4.7. A separation of the adsorbed enzymes can be effected by elution with N/10 phosphates at different p_H values at which one or other of the enzymes is destroyed. The proteinase can be obtained by elution at p_H 4.6, at which the peptidase is rapidly destroyed, while the latter enzyme is obtained by elution at p_H 9. A considerable destruction of both enzymes occurs in the process of isolation. Alternatively a cold water extract of green malt can be freed from proteinase by standing for several hours at ordinary temperature and at p_H 9, while the peptidase is destroyed by standing at 104° F. and p_H 4.6 for a few hours.

(133) Papain.

Another proteolytic enzyme which does not exist in malt, but which finds application in chill-proofing beer, may be mentioned here. This is papain, obtained from the unripe fruit of the Papaw tree. It differs from the animal proteolytic enzyme pepsin, which is active in acid solutions, in that it requires a neutral or alkaline reaction, but like pepsin it degrades the proteins of beer only as far as peptones. Pepsin is itself used for chill-proofing beers. The animal enzyme which carries the degradation further is known as trypsin. This acts optimally in alkaline solutions. The activity of papain may be increased some 200 or 300% by the presence of small quantities of cyanides (Section 124).

(134) Phosphatases.

Among other enzymes which play an important part in malting the phosphatases must be mentioned. The inorganic phosphates which are essential in yeast metabolism, fermentation and the buffering of wort are almost entirely derived from organically combined phosphorus in the barley. Four types of such enzymes have been described by Lüers and Malsch.¹³ Saccharophosphatase, which decomposes the phosphoric esters of the sugars; Glycerophosphatase, which acts on the glycerol phosphoric acid formed by the hydrolysis of lecithin and other phosphatides; Phytase, which converts phytin into the cyclic sugar inositol and phosphoric acid, and Nucleophosphatase, which sets free the phosphoric acid combined in nucleic acid. Optimal activities

§ 135 BIOCHEMISTRY OF MALT AND WORT

were found at 106°, 97°, 118° and 120° Fahr. and at p_H values of 6.0, 5.2, 5.3 and 5.6 for the respective enzymes. The phosphatase activity was found to increase during malting until it reached in green malt 8 to 11 times its value in barley. This activity is also increased more at low than high germination temperatures. The kilning process weakens them all.

(135) Lipase.

Malts may also be supposed to contain an enzyme or enzymes capable of hydrolysing fats. This activity has been ascribed to Lipase, but little is known of this enzyme in barley. The lipase of castor seed has, however, provided some suggestive indications of the course of enzymic increase during germination which have their applications to the theory of the development of diastatic activity in malt. In many cases an increase in enzyme activity is caused by proteolysis and can be imitated by the addition of protease, as will be shown with the diastase of barley. In the case of lipase the proteolysis appears to affect the protein carrier and becomes evident by a change of reaction most favourable for the action of the enzyme. The lipase of dormant castor seed hydrolyses fats best at p_H 4.7 and is inactive at p_H 7, while that of the germinated seed is quite active at p_H 7.

(136) Catalase.

The desmolases are a group of enzymes which differ from those which activate hydrolysis in that they appear to break the molecule acted upon by direct fission and are concerned in oxidation-reduction phenomena. Little is known of enzymes of this type in germinating barley. Catalase, which occurs in barley and has the power of splitting hydrogen peroxide, has been most fully studied. It is believed to be associated with metabolism and respiration in particular, thus taking a part in the germination of barley. It rapidly loses activity at p_H values below the optimum range of 7.0 to 7.7, so that its extraction and determination of its activity are carried out in 0.3N phosphate solutions at p_H 7.3 (K. and S. Myrbäck¹⁴). Its activity is measured in terms of the volume of oxygen liberated from hydrogen peroxide per unit of dry weight. This increases 10 to 40 times during germination, but 45–85% of the activity is destroyed during the kilning of Pilsener malt. Among the desmolases are also included aldehydrases, alcoholdehydrases, carbolicase, oxidases and peroxidases, zymase and carboxylase, which are dealt with in the sections on fermentation.

THEORIES OF THE NATURE OF DIASTASE

(137) α - and β -Amylase.

Ford and Guthrie¹⁵ found that extracts made by digesting finely ground barley for 20 hours at 86° Fahr. in water containing 1% of active papain, in presence of nitrobenzene to prevent the growth of micro-organisms, had a much greater converting power than similar extracts in water only. Thus the quantity of maltose produced from soluble starch was increased $2\frac{1}{2}$ and 3 times in particular cases, and was 5 times as great as that produced by a water extract at 64° Fahr. Intermediate values were obtained by digestions in presence of various salts, asparagine and boiled papain. This discovery provided the basis for much of the more recent work on the nature of barley diastase but various interpretations of the results are possible. The generally accepted conclusion is that part of the saccharifying enzyme present in barley exists in an inactive condition or in the form of an insoluble complex with proteins, from which it is liberated in an active, soluble state by maceration with proteolytic enzymes or during germination by similar enzymes present in the grain. According to this, no starch-converting enzyme is actually produced during germination, the increasing activity being due to the enzyme liberated by proteolysis and can go no further than corresponds with active and inactive enzymes already present in the barley.

Ohlsson¹⁶ prepared two distinct enzymes from cold water extracts of green malt. These he called Dextrinogenamylase and Saccharogenamylase but they are now generally known as α -amylase and β -amylase because the maltose first produced from soluble starch is in the α - and β - mutarotating forms (Section 109) respectively. They were separated from cold water extracts of malt by taking advantage of their varying resistance to temperature and hydrogen ions. β -amylase is more sensitive to heat and α -amylase more readily destroyed by acid. Thus α -amylase can be prepared free from β -amylase by heating and stirring the cold water extract of malt for 15 minutes at 158° Fahr. at p_H 6-7, while β -amylase is prepared by bringing the p_H value of the cold water extract to 3.3 at a temperature of 32° Fahr. by addition of N/10 HCl. Under these conditions α -amylase is rapidly destroyed so that after about 15 minutes β -amylase alone remains in the solution and can be preserved by restoring the p_H value to 6.0 by addition of phosphate buffer and keeping the extract on ice. The α -amylase preparation is stable under similar conditions. Optimum conditions for the activities of α - and β -amylase have been found to be as follows *in vitro* :—

§ 137 BIOCHEMISTRY OF MALT AND WORT

α -amylase	..	149° Fahr. and p_H 5·7
β -amylase	..	131° Fahr. and p_H 4·7

The properties of the two diastase fractions do not agree with the older view that malt diastase contains an amylase which decomposes starch to dextrins and a dextrinase which changes the dextrins to maltose. Ohlsson concluded that it contains two enzymes which act on starch simultaneously, but in a different manner. α -amylase gives products among which dextrins predominate, hence the name dextrinogenamylase or dextrin-forming amylase. He found that soluble starch solution undergoing conversions by this enzyme ceased to give a blue colour with iodine when only 11% of the starch was converted to maltose. Maltose is thus produced relatively slowly by this enzyme, as if it only resulted as a final product after repeated fission of the starch molecule and of the progressively shorter dextrin chains which were formed by each successive rupture. As a result short chain dextrins giving no colour with iodine would be produced in quantity before maltose appeared. β -amylase, on the other hand, destroys the iodine reaction relatively slowly, in the course of soluble starch conversion, as if maltose was successively split off from a residue of dextrins constantly diminishing in chain length. Maltose appears in comparatively greater quantities and hence the enzyme was called Saccharogenamylase or sugar-forming amylase.

The so-called Taka-diastase obtained from *Aspergillus oryzae* and other moulds and the starch-converting enzymes of the pancreas resemble α -amylase. Both α - and β -amylase have been found to exist in barley, the former almost entirely in an inactive state, though Myrbäck and Ohlssen have found that it sometimes occurs in small quantity in an active form. The soluble saccharifying diastase of barley is almost exclusively β -amylase. Hopkins, Cope and Green² prepared it by extracting 20 grams of finely ground barley in 60 ml. of 20% alcohol and, after filtering, making 30 ml. of the filtrate up to 100 ml. with 95% alcohol. The precipitated enzyme preparation is centrifuged out and can be dissolved in water. It is immaterial whether the barley extract is made with water or water containing papain. The active properties of the products are the same but the yield is substantially greater in presence of papain. β -amylase of barley was found to have most rapid saccharifying action on soluble starch at p_H 4·5–4·7 at 98·6° Fahr. At 136·4° Fahr., the greatest production of maltose in 30 minutes was at p_H 4·7. The enzyme was inactivated at p_H 8·0. The normal limit of maltose production of 60–65% is not substantially modified over the range of p_H 4·3–7·5.

Waldschmidt-Leitz, Reichel and Purr¹⁷ separated α - and β -amylase in green malt extracts adjusted to a p_H value of 3.8 by treatment with aluminium hydroxide, which adsorbs β -amylase, leaving the α -amylase in solution. Waldschmidt-Leitz also separated both the enzymes from barley extracts by adsorption methods. The preparation of α -amylase was, however, quite inactive until an activator also obtained from malt extracts was added. This activator, called amylo-kinase, was separated by Waldschmidt-Leitz and Purr¹⁸ from green malt extracts by adsorption on aluminium hydroxide. It was quite different from the enzymes and had no saccharifying activity but was destroyed by boiling for 30 minutes in neutral solutions. It was found to be different from the complement which Pringsheim extracted from yeast in that it was only able to accelerate the conversion of starch and did not carry the conversion beyond the usual resting stage. It cannot be dialysed and is apparently of high molecular complexity.

Waldschmidt-Leitz and Mayer¹⁹ have separated a third enzyme which liquefies starch paste but has no powers of saccharification. This they regard as a specific phosphatase and have named it amylo-phosphatase, suggesting the following explanation of the fall in viscosity of starch paste under its action. The phosphoric acid of starch may be esterically bound not to one but to two or three glucosidic chains, which it thereby unites in a larger colloidal starch unit. This, it may be imagined, is broken into two or three smaller units in the first stage of starch conversion by splitting off of the phosphoric acid which held together the molecular chains.

The relation between the diastatic enzymes of barley and malt may be summarised,²⁰ according to the investigations described, as follows :—

Amylophosphatase produced during germination.

In barley : Active and inactive β -amylase.

Inactive α -amylase.

Very small quantity of active α -amylase.

In malt : Active β -amylase.

α -amylase activated by amylokinase, possibly unknown activators.

The activation of dormant β -amylase during germination is caused by proteolytic enzymes which affect the protein-like colloidal carrier, an action which Ford and Guthrie showed could be imitated by extracting barley with a protease, e.g., papain. The course of the metabolic changes is thus represented firstly as an activation of proteinase which mobilises the protein-like

reserve substance, followed by attack and utilisation of the reserve carbohydrates of the grain. The conception of the production of amylokinase by proteinase during germination stresses the importance of activators which make it possible for the cell to benefit from quite different metabolic processes in an advantageous sequence. The activation of α -amylase may be supposed to result in the breakdown of large starch molecules into smaller fragments which greatly increase the number of points of attack for β -amylase, which is believed to split off maltose only from the ends of chains. This combined attack means a great increase of saccharifying activity during germination. Further it may perhaps be supposed that amylophosphatase plays some part in the early stages by bringing the starch into the necessary condition for attack by α -amylase.

(138) Sisto- and Eleuto-amylase.

This conception of the development of enzyme activity is not universally accepted and the present state of uncertainty in regard to the nature of diastase is made more apparent by the suggestion that its activity is determined not only by the presence of activators but, more particularly, by substances which inhibit its action. Chrzaszcz has interpreted the known facts on the basis that the activity of enzymes depends on their state of dispersion in a liquid and that "sisto-substances," which tend to convert them into an insoluble, inactive condition, exist in nature. The prefix "sisto" is derived from the German *sistieren*, meaning to stop or arrest. He holds that there are also "eleuto-substances," washing out or dissolving substances, which tend to counteract the action of sisto-substances and thus hold the enzymes in solution. Substances which act in these ways with amylase were called "sisto-amylase" and "eleuto-amylase."

Chrzaszcz and Janicki²¹ found that buckwheat malt had little or no diastatic activity but this was only apparent since the corns showed diastatic activity after the rootlets and acrospire had been removed. Ungerminated buckwheat has diastatic activity and the conclusion drawn was that sisto-substances were produced in the rootlets and acrospire during germination. The amylase of barley malt was, indeed, found to be paralysed by extraction in presence of the germs of buckwheat, or by shaking a filtered extract of malt for an hour with a preparation of the sisto-substance. If, however, peptone is added at the same time it renders the sisto-substance inactive or protects the amylase.

Chrzaszcz' view is that amylase development during germination depends on the production of a nitrogen-containing eleuto-substance by proteolytic action. The enzyme previously rendered

inactive by adsorption on sisto-substances becomes active through the ability of the soluble eleuto-substance, which may be a protein breakdown product, to eliminate the activity of the sisto-substance.

(139) Summary.

Enzymes are defined as catalysts of definite organic nature with specific activity, formed in living cells, but acting independently of the cells. Their chemical composition is unknown and they are only characterised by their activities. Comparative measurements of enzymic activity are usually made by determination of the quantity of products formed in a given time under strictly specified conditions. Enzymes are rapidly destroyed at temperatures considerably below the boiling point of water, and the extent of the changes they bring about depends on the balance between activation by rising temperature and destruction. The chemical reaction and enzyme destruction are both increased in speed by rising temperature to an optimum, time, hydrogen ion concentration and all other conditions being fixed. The optima for most enzymes lies between 100° and 130° in laboratory experiments, but are considerably higher when the quantity of water present is reduced, as in the mash tun or on the malt kiln. Under otherwise standardised conditions there is also an optimum hydrogen ion concentration for each enzyme. For diastase this is at about p_H 4.65 in dilute conversions at 70° Fahr., rising to about p_H 5.1 at 150° in a concentrated mash. p_H conditions are particularly important for proteolytic activity, in consequence of which it is sometimes necessary to increase the acidity of the mash.

The diastase of malt is believed to be a complex of several enzymes, but its actual nature and relation with the diastase of barley is still uncertain. Barley contains an active enzyme, usually known as β -amylase, which can saccharify soluble starch, but has very little liquefying power. Dormant β -amylase is activated during germination by proteolytic enzymes. α -amylase is also believed to exist in a dormant state, its activation during germination being possibly due to development of an activator, amylokinase. An amylophosphatase has also been detected in barley and malt and to it is attributed the first phase of starch breakdown. Their individual activities *in vitro* may be thus summarised. *Amylophosphatase* liquefies starch paste and liberates organically combined phosphorus. α -amylase appears to break starch primarily into reducing dextrins. β -amylase is the saccharifying enzyme measured by the Lintner method. It produces, from soluble starch, 60% of maltose and 40% of α -amylodextrin, which can be saccharified by α -amylase, leaving a resistant dextrin equivalent to 12% of the starch.

§ 139 BIOCHEMISTRY OF MALT AND WORT

Knowledge of the proteolytic and other enzymes of malt is even less advanced than that of diastase. The general opinion at present is that malt contains a proteinase and probably two peptidases. The proteinase appears to have far-reaching effects on the nitrogenous composition of wort and the quality of beer, but the peptidases probably have little action, if any, in the mash tun. The activity of the proteinase can be increased by suitable reduction in the p_H value of the mash. Cytase has important functions in the modification of malt by acting on hemicelluloses, phosphatases liberate phosphoric acid from organic combinations, and maltase may in some cases convert maltose to glucose in the mash.

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MALT

CHAPTER IX

FROM BARLEY TO MALT

CHANGES IN COMPOSITION DURING MALTING

(140) Composition of Malt.

The figures in Table 27 give a very generalised idea of the composition of malt and of the different proportions of certain constituents in two- and six-rowed types, in particular, the greater percentage of starch in the two-rowed and larger proportion of husk-forming materials, cellulose, lignin and hemicelluloses, in the six-rowed malts. Analyses such as these would be meaningless as an indication of the quality of malt without some knowledge of the physiological, physical and chemical changes in barley during malting. It is on these that the brewing value of malt depends in equal degree with the quality and composition of the barley and they are reviewed in this chapter as an essential introduction to the study of the finished material. Attention is confined to ordinary or white malts as distinct from coloured or roasted malts and special types which are dealt with in a later chapter.

TABLE 27.—CONSTITUENTS OF MALT

	Per cent.	
	Two-rowed	Six-rowed
Starch	58	53
Soluble carbohydrates	12	10
Hemicelluloses, pectins, etc.	7	10
Soluble pentosans	1	1
Cellulose and Lignin	6	10
Proteins (insol. $N \times 6.25$)	7	7
Soluble nitrogenous substances ($N \times 6.25$)	2.5	2
Fat	2	2
Tannin	0.3	0.5
Ash	2.2	2.5
Moisture	2	2

(141) Modification.

“ The one quality above all others which is required in a good

brewing barley is facility for ready and complete modification on the malting floor ; that is to say the starchy content of the endosperm must be reduced to a mealy consistency in order that the finished malt may possess sufficient friability and allow complete permeation of the coarsely crushed material with water during the mashing process so as to give full opportunities for the diastase to act on each individual starch grain. The more perfect the 'modification' has been, the nearer will the brewery extract approach the maximum which the material may be made to yield under the most favourable laboratory conditions for producing complete conversion of the starch." (H. T. Brown.¹)

This definition of modification emphasises the physical properties of friability which characterise a good malt, but the more modern tendency is to regard modification not merely from its physical aspects but as comprising all the changes in colloidal state and chemical composition which affect the constituents of barley during malting. It is the sum of all the changes from barley to malt. These are not confined to the period of germination but continue, under rather artificial conditions, during the early or drying stages on the kiln and materially influence the flavour and colour produced by curing at higher temperatures. The degree of modification or extent of these changes is of great importance in deciding the brewing quality of malt or the purpose for which it is suitable. The changes themselves are essentially of a physiological nature, the result of the action of enzymes, and it is difficult to reduce them to terms of chemistry or interpret them by ordinary analytical methods, but some of their effects can be followed by analysis and related to the quality of malt.

THE DEVELOPMENT OF ENZYMIC ACTIVITY DURING MALTING

(142) Changes in Diastatic Activity.

Determination of the enzymic activity of cold water extracts of barley and malt at various stages of germination and kilning is not a very satisfactory way of following its development during malting. A measure can be obtained in this way of some of its manifestations, but these can only imperfectly represent the motive power behind the physiological and chemical changes in germinating barley, and very incompletely assess the power of the enzymes to act on suitable substrates. The Lintner method, for example, only measures the extent of saccharification of soluble starch produced by a cold water extract of the malt, while the grains from the extraction, after thorough washing, contain sufficient

diastase to convert all their starch when mashed at 150° Fahr. The proteolytic enzymes similarly resist extraction by cold water, as shown by Kolbach and Simon's² curves in Fig. 33, which represent the effects of the soluble and insoluble enzymes by the quantity of permanently soluble and formol-nitrogen (1) in a cold water extract of a malt, (2) in a mash of the same malt made at 122° F., and (3) in a mash at 122° of the grains from (1). The points on the curves represent mgm. nitrogen in the extracts per 100 grams of dry malt substance.

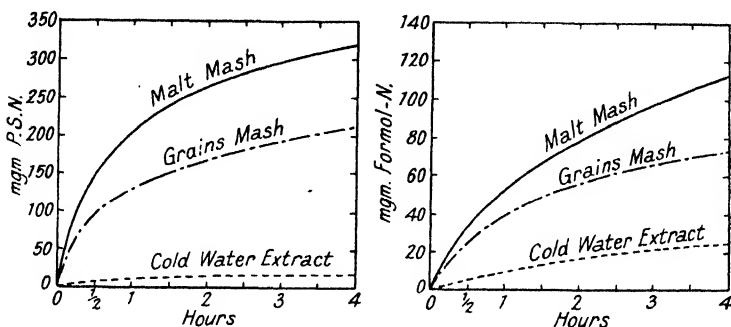


FIG. 33

EFFECTS OF SOLUBLE AND INSOLUBLE PROTEOLYTIC ENZYMES, SHOWN BY PRODUCTION OF P.S.N. AND FORMOL-NITROGEN (MGm. N PER 100 GRAMS DRY MALT SUBSTANCE)

Barley itself has a considerable diastatic activity, or power of saccharifying soluble starch, but only very slight ability to liquefy gelatinised starch. This is shown by the figures in Table 28, which represent analyses at various stages during malting. There is an initial period of slow enzyme development, usually extending over the first three days on the floor, followed by a rapid increase when growth is most active from the 4th to the 6th day or thereabouts. After this there may be a slight rise, a stationary period or even a small decrease during the last day or two on the floor, according to the conditions of germination, with secondary increases if growth is stimulated by sprinkling. The rising temperature in the very early stages of kilning may occasion a further slight increase in diastatic activity, but this is soon followed by a gradual fall, which becomes more marked when the temperature is raised for curing.

It is frequently assumed that a reasonably approximate idea of the activity of other enzymes in malt can be gained from determination of the "diastatic activity," but the examples given in Tables 28 and 31 show that this is not strictly true. Fletcher and Westwood,³ from whose analyses the figures for the Scotch malt are derived, measured the "dextrinolytic" and "liquefying"

functions of the diastase as well as the saccharifying activity, using a preparation of Baker's α -amylodextrin as substrate for the first. It will be noted that development of the so-called dextrinolytic activity is not parallel with the saccharifying function, and that the great increase of liquefying power comes considerably later on the floor, and that it is more resistant on the kiln.

TABLE 28.—CHANGES IN ENZYMIC ACTIVITY DURING MALTING

Barley	Lincolnshire	Scotch		
		Gms. maltose produced by aqueous extract of 1 gm. dry grain in 1 hr. at 45° C.		Liquefying power Gms. gelatinised starch liquefied by aqueous extract of 1 gm. dry grain in 1 hr. at 21° C.
		From soluble starch	from α -amylodextrin	
Original barley ..	48	—	0.4	4
On floor 1st day ..	52	—	—	1
„ 2nd „ ..	61	—	—	1
„ 3rd „ ..	82	6.6	0.5	1
„ 4th „ ..	126	7.5	1.4	13
„ 5th „ ..	125	12.1	2.5	42
„ 6th „ ..	141 (sprinkle)	11.9	4.2	116
„ 7th „ ..	141	16.1	4.9	140
„ 8th „ ..	139	16.9	5.4	168
„ 9th „ ..	136	14.8	6.6	174
„ 10th „ ..	—	17.4	6.3	178
„ 11th „ ..	—	17.5	6.8	160
On kiln 1st „ ..	140	10.3 (hand dry)	5.1	168
„ 2nd „ ..	133	6.4 (12 hrs. after)	3.6	214
„ 3rd „ ..	104	7.2 (36 „ „)	3.2	208
„ 4th „ ..	53	5.3 (48 „ „)	2.6	214
Finished malt ..	32	5.8	2.5	210

There can be no definite relation between the diastatic activity of barley and malt on account of variations in its development during germination and destruction on the kiln, but, as a general rule, the diastatic activity of malt from the same variety of barley, malted in a similar manner, increases with the nitrogen content. Some analyses⁴ of Plumage-Archer barleys and malts are given in Table 29.

TABLE 29.—DIASTATIC ACTIVITIES OF PLUMAGE-ARCHER BARLEYS AND MALTS

Nitrogen % dry barley	Diastatic activity, Lintner°		Colour of malt
	Barley	Malt	
1.44	27.5	36.0	3.9
1.55	40.5	36.6	5.0
1.65	32.0	42.0	4.9
1.77	38.5	41.3	4.1
1.92	40.0	45.0	6.1

K. and S. Myrbäck⁵ took advantage of Ford and Guthrie's discovery that more diastase could be extracted from barley by maceration in presence of a proteolytic enzyme than by extraction in cold water to follow the liberation of the inactive β -amylase, which is believed to exist in barley together with the free or water-soluble β -amylase. They determined the saccharifying activity of cold water extracts and of extracts obtained by digestion for 20 hrs. in a 0.25% solution of papain. The difference in the maltose produced represents the activity of the liberated enzyme. They also determined the rate at which the starch conversions lost their power of giving a blue colour with iodine, which they held to be an indication of the quantity of α -amylase present, as it was liberated or rendered active during malting. Their results with a Swedish barley in Table 30 show that the whole of the latent β -amylase becomes free or soluble about the 6th day on the floor.

TABLE 30.—CHANGES IN AMYLASE ACTIVITY DURING MALTING

	Blue iodine reaction lost in	β -Amylase activity mgm. maltose per minute from 1 gm. grain	
		Free	Total (with papain)
Original barley ..	More than 48 hours	15.8	18.9
Steeped barley ..	" " 24 "	13.6	20.9
Malted 2 days ..	About 20 minutes	14.9	20.9
" 4 " ..	" 30 "	21.6	22.1
" 6 " ..	" 15 "	24.4	24.5

They concluded that there was a rapid increase of α -amylase during the first day or two of germination, and, later, the latent β -amylase of the barley became active under the influence of proteolytic enzymes, as shown by the decreasing difference between the total and free enzyme. Though the maltose production is ascribed to β -amylase in the Table, a small proportion of it is no doubt due to the α -amylase.

(143) Proteolytic Enzymes.

It is more difficult to follow the changes in proteolytic activity on account of the lack of satisfactory methods of analysis. Methods involving measurements of the rate of change in the viscosity of gelatine solutions, titration in alcoholic solution of the COOH groups produced by hydrolysis of edestin or based on estimation of the permanently soluble and formol nitrogen in extracts of malt

made at 32° F., and in the wort from the laboratory hot mash are available. The difference between results obtained with hot and cold extracts expressed as a percentage of the total nitrogen of the malt represents proteinase, and, possibly, peptidase action on the malt proteins in the mash tun. These three methods rarely give concordant results, as the analyses by Laufer⁶ abstracted in Table 31 show, but they are sufficiently indicative to show that the diastatic and proteolytic activities of malts are not necessarily parallel.

TABLE 31.—DIASTATIC AND PROTEOLYTIC ACTIVITIES OF MALTS

Malts	Manchuria and Oderbrucher				Pacific Coast		European two-rowed	
Diastatic activity, Lintner ..	120	128	125	149	99	39	66	71
Proteolytic units, 100 gms. dry malt—								
(a) Viscosity	96.3	68.2	68.0	95.1	74.0	34.0	74.7	74.8
(b) Edestin titration ..	47.0	45.0	39.8	51.1	39.4	31.8	52.0	51.2
Increase from cold to hot mash in 100 gms. dry malt—								
(c) P.S.N. as % of total N	9.1	11.5	14.2	15.7	14.4	2.7	17.4	18.5
(d) Formol-N % of total N	1.9	7.0	3.9	3.9	3.2	0.3	3.0	4.2

(144) Development of Cytase during Malting.

Changes in the hemicellulose constituents of barley are among the most important that occur during malting. These are attributed to the little-known group of enzymes denoted by Cytase and are reflected by reduction in the viscosity of laboratory hot extracts of malt at progressive stages of germination. Piratzky and Wiecha⁷ have studied the development of the enzymes concerned, by using the very viscous extract from a slightly grown or chit malt as substrate and measuring the reduction in viscosity, caused by cold water extracts of malt, by means of a falling sphere viscometer. The percentage reduction was divided by the dry weight of the grain used, giving results which are of particular interest in connection with the progress of modification, Table 32.

It will be noticed that the enzymes concerned in the reduction of viscosity, like others, attain nearly maximum activity by about the fifth day of germination and are much more resistant to kiln treatment than the diastase, as measured in cold water extracts. The influence of kilning conditions on the destruction of enzymes is very clearly shown by comparison of these figures with those in Table 33 by the same authors. Increase of temperature has a much greater restrictive effect on the enzymes, if it is allowed to take place when the moisture content of the malt is compara-

tively high. The figures in Table 32 refer to a dark malt in which the moisture was only reduced to 15% on the top floor of the kiln. Those in Table 33 are from analyses of a pale malt in which the moisture content was brought down to 5% on the upper floor, the temperature being only slightly lower. The final temperatures were, dark malt 234° Fahr., pale malt 184° Fahr.

TABLE 32.—CHANGES IN THE ACTIVITIES OF DIASTASE AND CYTASE DURING MALTING (DARK MALT)

	Moisture % of malt	Diastatic activity Windisch- Kolbach	Cytase activity		
			Malt used dry weight gm. (<i>m</i>)	Viscosity reduction % (<i>a</i>)	$\frac{a}{m}$
Germinated 3 days ..	41.8	116.7	0.383	38.0	99.3
" 5 " ..	39.7	291.0	0.390	71.6	183.6
" 7 " ..	39.3	347.0	0.396	73.6	185.8
" 9 " ..	38.9	355.0	0.395	76.8	194.3
Kiln, upper floor ..	15.0	289.0	0.568	74.2	130.7
" lower floor ..	3.1	201.1	0.658	74.5	113.3
" cured ..	1.3	68.7	0.672	67.0	99.7

TABLE 33.—CHANGES IN THE ACTIVITIES OF DIASTASE AND CYTASE DURING MALTING (PALE MALT)

Sample	Moisture % in sample	Diastatic activity (W-K)	Cytase activity		
			Weight used, grams (<i>m</i>)	Viscosity reduction % (<i>a</i>)	$\frac{a}{m}$
Barley	15.9	98.7	0.561	36.4	64.9
Steeped barley ..	44.8	31.8	0.354	21.7	61.2
Germination, 60 hrs.	42.5	81.3	0.371	25.2	67.9
" 7 days	39.7	363.0	0.390	77.4	198.4
Kilned, upper floor ..	5.55	324.5	0.213	36.1	169.2
" lower floor ..	2.99	232.0	0.219	30.3	138.2

Piratzky and Wiecha found that the viscosity of worts could not be reduced by starch-converting or proteolytic enzymes, though most diastatic preparations contain some of the enzyme in question. They therefore concluded that it was not due to starch or proteins. The optimum temperature and p_H conditions for viscosity reduction also closely corresponded with those attributed to cytase,⁸ making it highly probable that the viscosity is due to products of the incomplete breakdown of the cell walls, that is of hemicelluloses or pectinous substances.

CHANGES IN BARLEY COMPOSITION DURING MALTING

(145) Balance between Enzymic Breakdown and Synthesis during Malting.

The simplest way to follow the chemical changes which occur during malting is by analysis of the soluble products of enzymic change at various stages. But here a difficulty arises in that the soluble substances at any moment during the life of the grain are not in a static condition. The quantity found is the result of a balance between enzymic breakdown and synthesis.¹⁸ In the downgrade processes complex materials, starch, protein, etc., are rendered soluble and diffusible, while in the upgrade processes the simple soluble substances which have passed through the cell walls into the embryo are built up again by enzymes into substances which are the same or very similar to those from which the diffusible substances originated. This point is emphasised on account of its importance in the interpretation of the analytical results. The latter merely give the quantity of soluble substance at the moment at which metabolism was arrested. Some of the soluble matter represents downgrade products, some is at its ultimate state of simplification, while some exists in intermediate stages of the upgrade processes. There is no means of differentiating between these fractions of the soluble matter and no information on how variations in their respective quantities influence the quality of malt.

A similar difficulty exists in regard to the significance of the insoluble parts of the grain. Some of the tissues built up in the embryo and rootlets are possibly very similar or identical in composition with those of the endosperm from which they were derived, but the composition of the rootlets is very different from that of the rest of the corn. The same, no doubt, applies to the new tissues of the embryo and acrospire. Even if parts of them are similar in chemical composition, they may be very different in colloidal state or properties from corresponding substances in the endosperm. Despite the uncertainty which exists in regard to the interpretation of analyses, there is much evidence relating the quantity of the soluble substances in malt with its brewing quality. This quantity represents the balance between the two processes of breakdown and synthesis and there is little doubt that the nature of the substances comprised in it will ultimately prove to be the significant factor in quality, in so far as this depends on the soluble constituents of malt.

THE CARBOHYDRATES OF MALT

(146) Starch.

The starch of malt appears to be identical with that of barley, though the granules are slightly corroded during malting. This enzymic attack is apparently accompanied by some change in its physical or colloidal state, making the starch of malt more readily convertible to dextrin and sugars, although it still remains insoluble in cold water. The extract of malt is derived mainly from the starch but other constituents capable of conversion to soluble products in the mash or existing in the malt in a soluble form contribute their share. There is consequently no direct relation between the extract and the quantity of starch in the malt. The starch of barley is not converted by diastase unless previously gelatinised but as germination proceeds it becomes progressively more readily converted. In barley and during the early stages of germination the starch granules are embedded in a resistant matrix of protein and other substances and cannot be extracted unless the grain is very finely ground. As germination proceeds this matrix is disintegrated and the extract obtainable from the coarsely-ground malt increases. This is shown in Table 55. There comes a time, however, if germination is prolonged, when the extract falls instead of rising. This is due to loss by respiration which affects the carbohydrate constituents of barley.

The relation of extract, as determined by ordinary methods of mashing, with the progress of germination is thus complicated. The starch becomes gradually more amenable to conversion by the enzymes which are being activated at the same time, not only on account of change in its own physical state but also through disintegration of the matrix in which it exists in the barley. The quantity of starch in the malt is also being continually reduced by respiration. Since extract is measured by the relation between the soluble substances in the wort and the total weight of the malt, its increase depends both on the increase of soluble or convertible substances and decrease of total dry weight, but since respiration loss, which causes the latter, is due mainly to destruction of starch, its ultimate effect is that the relation of soluble to insoluble substance, and consequently extract, decreases.

The effect of modification on extract may be judged by comparison of the extract obtained by one of the standard methods of analysis and the "total available extract" of the sample, after gelatinisation and conversion with diastase, as in the analysis of raw grain. Figures showing this are given in Table 49. There was progressively closer correspondence as germination proceeded

and higher results were found, when the malting was carried out between 55° and 59° Fahr., than when the floor temperatures were between 64.5° and 70° Fahr.

(147) Cold Water Extract of Malt.

By cold water extract is meant the quantity of solid matter extracted from barley or malt by macerating the ground grain in cold water for a specified time, usually three hours. Since the soluble enzymes are extracted it is desirable to use water at about 32° Fahr. to prevent enzymic action when a precise determination of the soluble matter present in malt is required. The cold water extract of barley varies in quantity and may be between 5 and 10% of its dry weight. This is reduced by about 2 or 3% in the steep, the loss of solid matter being due to extraction from the husks, as the semi-permeable membrane prevents extraction from the parts within it. Samples taken daily during malting show a slow increase in cold water extract during the first day or two on the floor, followed by a rapid increase during the period of greatest germinative activity, extending over three or four days. After this there is generally a slow increase until the close of germination, in general agreement with the figures given for the development of enzymic activity. The changes vary with the germinative activity of the barley and the malting conditions. In some cases there is an increase up to about the seventh day on the floor, followed by a decrease of about 1%, while activation of germination by sprinkling may cause small increases. An example of the course of events with a lager malt is given in Table 41. The increase in cold water extract during flooring of an English malt is very similar but the final quantity usually reaches 18 to 20%, while that of English-made Californian and other malts from similar six-rowed barleys is generally between 15 and 17%.

Enzymic breakdown continues on the kiln if the temperature and moisture conditions are favourable. The changes in cold water extract are slight if the malt is dried rapidly at a comparatively low temperature but the increase may be considerable if it is held at about 120° to 130° Fahr. for any length of time when the moisture content is above 20%. The influences of temperature and moisture are rather complicated in conjunction one with the other. Increase of temperature activates enzymes but destruction becomes more rapid at the same time. Reduction of moisture has a retarding influence on enzymic change but the enzyme is more rapidly destroyed in presence of more water. Unduly high percentages of cold water extract produced by stewing or forcing on the kiln are held to indicate changes which are detrimental to the quality of malt and stability of the beer (Section 176).

A moderate increase in reducing sugars and amino-acids is required in order to produce by condensation during curing the dark, aromatic melanoidins (Section 209) which give the flavour and colour to dark malts. For this reason it is usual to raise the temperature with these malts when the moisture content is comparatively high to encourage enzymic breakdown to the desired extent. Kolbach and Schild⁹ found that starch breakdown with malt containing 23% of moisture was most rapid at 158° Fahr. This is considerably higher than the optimum for starch conversion in the mash tun on account of the greater concentration of substrate relative to water on the kiln. As the temperature rises and moisture content falls there is generally a reduction in soluble products, as shown in Fig. 34, from analyses by Siau and Hodson.¹⁰

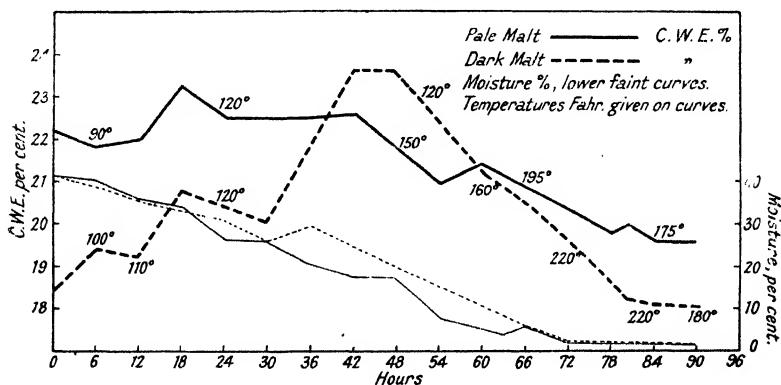


FIG. 34
CHANGES IN COLD WATER EXTRACT AND MOISTURE ON KILN

(148) Sugars of Malt.

About three-quarters of the cold water extract of malt consists of carbohydrates, a considerable proportion in the form of "ready-formed sugars." It also includes products of proteolytic breakdown, accounting for some 3 or 4% of the dry weight of the malt, and soluble salts amounting to 1 or 2%. A small proportion is also due to breakdown products of the pentosans or hemicellulosic tissues of the grain. Examples of analyses by Wright¹¹ of the "ready-formed sugars" in English malts and barley are given in Table 34.

The sucrose, glucose and fructose were extracted by 70% alcohol, identified and estimated by the formation of osazones and by optical activity and reducing power. The sugars referred to as "A," "B," and "C" were not definitely identified, but were apparently a series of polysaccharides, among which was a possible trisaccharide of the structure glucose-fructose-galactose. The "A" sugars constituted the residue left after fermentation of

TABLE 34.—SUGARS IN ENGLISH BARLEY AND MALTS
(PER CENT ON DRY MATTER)

	Malt 1	Malt 2	Malt 3	Barley
Sucrose	4.17	4.63	4.01	0.76
Glucose	0.84	—	—	—
Fructose	1.86	2.00	2.03	0.25
"A" sugars as trisaccharide ..	1.97	2.43	3.96	—
"B" sugars } as glucose of	1.14	0.71	1.51	0.20
"C" sugars } hydrolysis	3.45	2.22	3.24	0.04
	13.43	11.99	14.75	1.25

the sugars extracted by alcohol by *Saccharomyces exiguus*. They were fermentable by *S. cerevisiæ*, and on hydrolysis gave glucose and fructose approximately in the ratio 2 : 1. The "B" and "C" sugars were extracted by water from the grains left after alcoholic extraction. The "B" sugars were fermentable by *S. exiguus*, while the "C" sugars were not fermented by this yeast but were fermentable by *S. cerevisiæ*. The sugars fermentable by *S. cerevisiæ* but not by *S. exiguus* had previously been assumed to be maltose, but Wright could obtain no evidence of the presence of this sugar. The non-occurrence of maltose in malt is striking. It is apparently hydrolysed to glucose, possibly by maltase. Sucrose is the predominant sugar and is probably synthesised from glucose and fructose to form the chief reserve sugar, as is the case in many other plants.

Various changes occur among the sugars during kilning according to the conditions of temperature and moisture content. The cane sugar usually increases in quantity, while the reducing sugars may fall continuously or rise at lower temperatures and subsequently fall at higher temperatures by condensation with amino-acids to form melanoidins. This fall is slight in pale malts, but greater in full-flavoured dark malts. Lüers and Nishimura gave the following analyses of pale and dark malts, Table 35.

TABLE 35.—CHANGES IN SUGARS DURING KILNING

	Pale malts				Dark Malt	
	A		B		Invert %	Cane %
	Invert %	Cane %	Invert %	Cane %		
Green malt	2.25	3.96	2.94	4.30	2.77	4.64
On removal to lower kiln floor ..	—	—	—	—	2.42	5.18
Finished malt	2.21	4.22	2.62	4.84	2.15	5.40

(149) Changes in the Hemicelluloses during Malting.

It is possible that measurement of the breakdown of hemicellulose might prove useful as an indication of the extent of attack on the cell walls implied in the original but restricted physical conception of modification. Lüers and Loibl suggested that the quantity of soluble pentosans extractable from malt might be used to measure the extent of cytase action and thereby afford an Index of Modification. This was tested by Fink and Hartmann¹² by analyses of samples from a malt at various stages of growth and kilning, using the barbituric acid method of furfural determination. The figures in Table 36 show the total pentosan in 100 grams of dry malt substance, the soluble pentosans and the latter expressed as a percentage of the total pentosans.

TABLE 36.—CHANGES IN TOTAL AND SOLUBLE PENTOSANS DURING MALTING

	Total pentosans % on dry substance	Soluble pentosans % on dry substance	Soluble pentosans % of total
Barley	8.3	0.25	3.0
„ steeped	8.5	0.20	2.4
Floor, 1st day	8.7	0.22	2.5
„ 3rd day	8.8	0.52	5.9
„ 4th day	8.8	0.78	8.9
„ 5th day	8.7	0.90	10.3
„ 7th day	9.3	0.98	10.7
Kiln, upper floor	9.3	1.00	10.8
„ lower floor	9.4	1.05	11.2

These results give an indication of the quantity of hemicellulose existing in the malt at each stage as well as of its breakdown products, and, though cytase appears to be most active about the 3rd, 4th and 5th days on the floor, after which equilibrium occurs through utilisation of soluble pentosan by the rootlets and acrospire, there are signs of continued breakdown with increasing modification. Little is known of the effect of soluble pentosans or pentose sugars on the brewing quality of malt, but it would appear probable that they influence such properties as palate-fulness and head retention. Among analyses published by Fink,¹³ a poorly modified malt showed a pentosan value (soluble pentosans as % of total pentosans) of 9.2, while a well-modified malt gave 9.8%, a very well-modified malt 12.0%, a crystal malt 8.8%.

THE NITROGEN OF MALT

(150) Migration of Nitrogen during Malting.

Part of the proteins of the endosperm of barley is broken down during malting to simple, soluble products which are transferred by diffusion through the cell walls to the embryo, where they are utilised in resynthesis of proteins in the acrospire and rootlets. The results of this migration of nitrogen to the growing parts of the grain are illustrated in Table 37 by Brown's ¹⁴ figures for the relative weights and nitrogen content of separated endosperms, germs and rootlets. The acrospires are included with the germs and the husks with the endosperms. The total nitrogen content of the barley was 1.479% on its dry weight, whereas a sample of the excised germs contained 4.94% of nitrogen on dry matter.

TABLE 37.—WEIGHT AND NITROGEN CONTENT OF ENDOSPERM, GERM AND ROOTLETS

	Distribution of Mass			Distribution of Nitrogen		
	Endo-sperm	Germ	Rootlets	Endo-sperm	Germ	Rootlets
Barley, steeped ..	96.4	3.6	—	86.6	13.4	—
Malt, 5 days ..	92.4	4.3	3.3	72.8	18.1	9.1
„ 11 days ..	82.6	13.0	4.4	51.5	36.3	12.2

The finished malt, deprived of its rootlets, gave the following figures :—

Weight of endosperm	86.5 per cent.
„ germ	13.5 „
	<u>100.0</u>
Nitrogen in endosperm	58.7 „
„ germ	41.3 „
	<u>100.0</u>

(151) Nitrogen Content of Barley and Malt.

There is a small loss of nitrogen during steeping, which may amount to about 1% of the nitrogen originally present in the barley, but there is no further loss by respiration during germination, as can be shown by determining the weight of nitrogen in 1,000 corns of the steeped barley and malt with rootlets. This figure is not the same as the percentage of nitrogen in the malt, but the

latter usually differs but little from that in the barley, when both are expressed on dry matter, although such a large proportion of the original nitrogen of the barley is removed with the rootlets, about $\frac{1}{8}$ in the above example. This is because there is an almost proportional loss of the total dry matter on which the nitrogen percentage is calculated. The loss of dry matter by extraction in the steep, respiration and removal of rootlets is known as the "malting loss" and is expressed as a percentage on the dry weight of the original barley. The difference between the nitrogen content of barley and malt is commonly about 0.05%, when both are expressed as percentages on dry matter, but in some cases the nitrogen content of the malt is slightly higher than that of the barley. This is the case if the total loss of dry matter is proportionally greater than that of the nitrogen, as it may be if respiration loss is high.

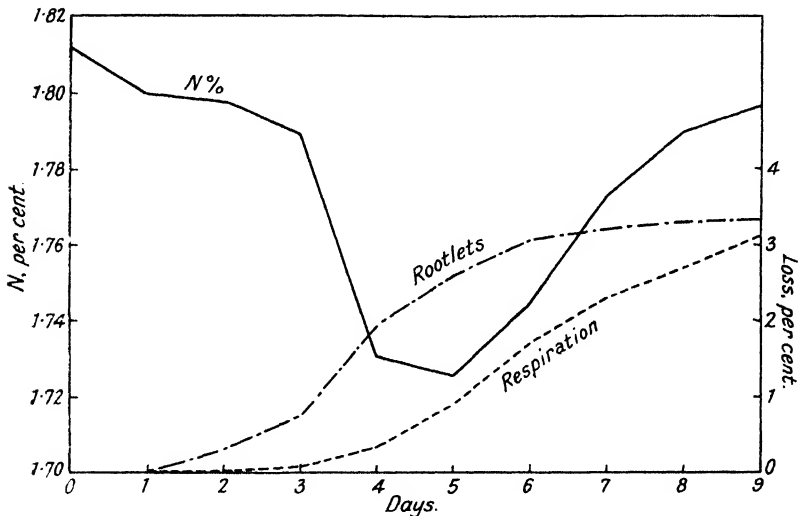


FIG. 35
CHANGES IN NITROGEN CONTENT OF BARLEY DURING GERMINATION
(PERCENTAGES ON DRY WEIGHT)

The diagram in Fig. 35 by Piratzky and Rehberg,¹⁵ representing analyses of samples taken daily from a growing piece, is given as an example of the effects of rootlet growth and respiration loss on the nitrogen content of malt. In this case the nitrogen loss outstripped the total loss of dry matter during the early stages of germination when rootlet growth was comparatively rapid. As a result the nitrogen content fell. Later the total loss of dry matter was proportionally less than rootlet growth, and the nitrogen percentage increased until it had regained almost its original figure. The figures for loss are percentages of dry

matter lost in rootlets and respiration. The 1,000-corn dry weight fell from 40.1 to 37.5 grams.

(152) The Proteins of Malt.

Osborne and Campbell¹⁶ showed that malt contained four proteins similar to those of barley, but they thought that the alcohol-soluble protein of malt was different from that of barley and called it Bynin. Schjerning followed Osborne in holding that hordein was first partly converted to a soluble protein giving reactions similar to those of the second of the two soluble proteins, Albumin 1 and Albumin 2, which he believed existed in barley and identified with Osborne's leucosin and edestin respectively. The former is an albumin, the latter a globulin. More recent analyses by Bishop¹⁷ point to the identity of the alcohol-soluble proteins of barley and malt and he consequently proposed that the term bynin should be abandoned.

Bishop¹⁸ applied the method of protein separation found useful with barley to samples of malt taken at intervals from a growing piece. An example of his results is given in Table 38. Three fairly well-defined stages can be distinguished, corresponding with those found for the development of enzyme activity and in the breakdown of hemicellulose. Very little change took place during the first two days on the floor, but during the next four days there was a rapid attack on the hordein and glutelin accompanied by increase in the salt-soluble nitrogen or that part of it represented by degradation products of the proteins and given in the columns headed non-protein nitrogen and proteose. No change was found in the albumin and very little in the globulin. There was little change in any of the fractions during the remainder of the time on the floor. The times given in the Table represent hours from the commencement of steeping.

TABLE 38.—CHANGES IN THE PROTEINS OF BARLEY DURING MALTING
BARLEY—GARTON'S IMPROVED
(NITROGEN GM. PER 100 GM. DRY WEIGHT)

			Total Nitro- gen	Salt- soluble	Hor- dein	Glu- telin	Albu- min	Non- protein	Total Protein	Glo- bulin	Pro- teose
0 hours	1.703	0.563	.631	.509	.186	.130	.345	.159	.093
60	"	..	1.740	0.502	.632	.606	.132	.152	.266	.134	.079
120	"	..	1.688	0.508	.601	.579	.129	.195	.243	.114	.072
170	"	..	1.611	0.743	.430	.438	.190	.318	.266	.076	.155
216	"	..	1.667	1.025	.286	.356	.179	.549	.366	.187	.062
312	"	..	1.662	1.031	.253	.378	.171	.532	.322	.151	.170
340 on kiln											
364 hours	1.689	1.072	.270	.347	.176	.525	.399	.223	.150
406	"	..	1.684	1.048	.261	.375	.183	.546	.393	.210	.198
456	"	..	1.597	0.935	.269	.393	.184	.507	—	—	—
Malt without rootlets											

The results suggest that the degradation of proteins in the endosperm and the upgrade processes in the growing plant reach a state of approximate balance during the later part of the flooring period. This can be seen more clearly if the results are expressed as weights of nitrogen per 1,000 corns, in which manner the changes in the three main fractions in another barley are shown in Fig. 36. The decrease in hordein and glutelin during the first seven days on the floor is here balanced by increase in salt-soluble nitrogen, which includes the albumin, globulin, proteose and non-protein nitrogen. The last represents nitrogen in the simpler digestion products, together with small quantities of organic

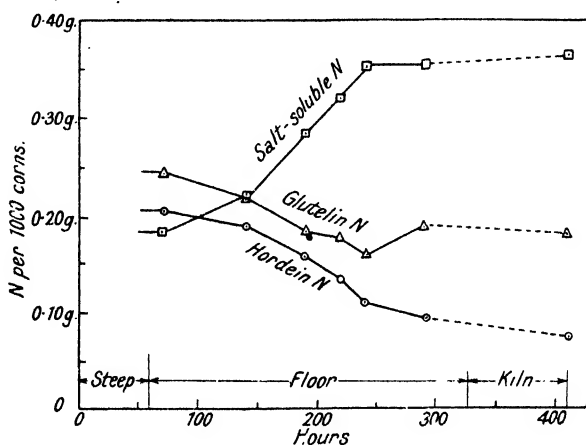


FIG. 36
CHANGES IN MAIN NITROGEN FRACTIONS DURING MALTING

bases, such as betaine, choline and hordenin. It will be noticed that the salt-soluble nitrogen increased from 33.6% of the total nitrogen of the barley to nearly 55% in the malt or 62% of the total nitrogen of malt and rootlets. The excess of breakdown over synthesis is shown by the difference between the sum of the proteose and non-protein nitrogen in malt and barley respectively. Very little change in nitrogen distribution was found to occur during kilning of pale malts. The greatest change from barley to malt is shown by the hordein.

(153) Proteins of Six-rowed Malts.

The few analyses of six-rowed malts available indicate that a difference exists between the two- and six-rowed malts in respect of the proportions of the original barley proteins broken down, and particularly in the production of a smaller quantity of salt-soluble and non-protein nitrogen in the six-rowed. The analyses

by Rose and Anderson¹⁰ in Table 39 refer to a Manchuria barley O.A.C.21, and its malt. The barley contained 2.19% of nitrogen and gave a malt with 2.20%, both on dry matter. The thousand-corn weights were 32.4 and 29.4 respectively. These analyses are interesting from the light they throw on the effects of malting on different parts of the corn and on the nature of the protein synthesised in the acrospire in which there was also an accumulation of intermediate products or non-protein nitrogen. The newly-formed protein was found to be a glutelin, which Rose and Anderson concluded was different from the insoluble protein of the endosperm and, probably, a distinct protein.

TABLE 39.—CHANGES IN THE PROTEINS OF SIX-ROWED BARLEY DURING MALTING. O.A.C.21

A = Nitrogen, mgm. per 1,000 corns.

B = Nitrogen of fractions as % of total nitrogen.

	Barley				Malt			
	Endo-sperm	Husk	Embryo	Total	Endo-sperm	Husk	Embryo	Total
A								
Non-protein ..	53	5	6	64	117	7	16	140
Water-soluble ..	58	2	11	71	91	1	11	103
5% K ₂ SO ₄ sol. ..	87	0	3	90	81	0	3	84
Hot 70% alcohol ..	253	1	3	257	158	1	4	163
Residue (glutelin) ..	203	8	17	228	118	7	41	166
	654	16	40	710	565	16	75	656
B								
Non-protein ..	8	31	16	9	21	43	22	21
Water-soluble ..	9	13	28	10	16	7	15	16
5% K ₂ SO ₄ sol. ..	13	0	7	13	14	2	4	13
Hot 70% alcohol ..	39	6	6	36	28	9	5	25
Residue (glutelin) ..	31	50	43	32	21	39	54	25

(154) Hordein of Malt.

The progressive breakdown of hordein and glutelin during the first half of the flooring period suggests that information on the modification of malt could be obtained by their estimation. Of these, hordein is the more readily determined, and, being apparently a definite substance, its estimation would appear to be more satisfactory than that of such indefinite products as permanently soluble or formol nitrogen. By comparing malts with similar nitrogen content Lüers and Geiger²⁰ found that higher hordein or hordein nitrogen expressed as a percentage on total nitrogen did correspond with reduced modification as indicated by acrospire length. Examples of analyses of English-made malts by Lüers and Hind in Table 40 show that results obtained in this way correspond with the indications given by the cold water extract

and permanently soluble nitrogen. The figures for the Californian malt cannot be compared with those for the English malts on account of the reduced breakdown in six-rowed malts. It must also be remembered that barleys with a greater nitrogen content contain a greater proportion of hordein than low nitrogen barleys, so that a greater proportion of hordein in malt does not necessarily mean reduced breakdown.

TABLE 40.—HORDEIN NITROGEN OF ENGLISH-MADE MALTS
(PERCENTAGE ON DRY SUBSTANCE)

Barley	Extract lb.	Total N %	P.S.N. %	P.S.N. % of total N	C.W.E. %	Acrospire							Hordein N as % of Total N
						0	- 1	1	2	3	4	5	
Somerset ..	100.0	1.40	0.55	39.3	19.5	-	-	-	6	91	2	1	21.85
Scottish ..	98.7	1.48	0.54	36.5	18.2	2	-	-	30	68	-	-	24.93
Norfolk ..	97.7	1.58	0.54	34.2	17.9	3	-	1	21	73	2	-	26.76
Californian ..	94.5	1.41	0.41	29.1	15.4	-	-	8	58	32	1	-	23.27

(155) Products of Protein Breakdown.

A considerable proportion of the original protein constituents of barley is altered to such an extent by proteolytic enzymes during malting as to form compounds belonging to the simpler groups known as metaproteins, proteoses, peptones, polypeptides, amino-acids and amides. It would appear that the embryo is nourished mainly by amino-acids, which resemble the simple sugars in their ability to diffuse through the cell walls, but the greater proportion of the nitrogen in the simplest combinations is built up into asparagine (amino-succinamic acid, $C_2H_3 \cdot NH_2(COOH)CO \cdot NH_2$) in malt in a manner corresponding with the synthesis of cane sugar from hexoses. Little is known of the nature of the individual protein degradation products in malt, but Schild²¹ came to the conclusion, though this must be regarded as rather tentative, that barley contains little or no polypeptides, but that these accumulate in malt as a result of the very energetic proteolytic action which occurs after the slow commencement of germination and lasts until about the 5th or 6th day. He ascribed the rapid increase of formol-nitrogen that occurs during that period to polypeptides and not to the accumulation of amino-acids, the greater part of which is utilised as formed by the growing embryo.

It is particularly important that an extract of malt used for determination of nitrogen existing in a soluble form should be made in water at about 32° Fahr. as proteolysis occurs at comparatively low temperatures. Schild's figures in Table 41 showing the changes in composition of samples taken daily during germination

were obtained from 10% extracts in water at 32°. A small quantity of the malt was kept on the floor for two extra days after the bulk was loaded to kiln to show the effect of over-modification. The barley contained 1.867% of nitrogen on dry matter and was malted according to the Munich method for dark malt.

TABLE 41.—CHANGES IN COLD WATER EXTRACT AND COLD WATER SOLUBLE NITROGEN DURING MALTING. MUNICH MALT
(N AS MGMS. PER 100 GRAMS DRY MATTER)

	Barley		Days on Floor								Over-Grown		Kilned
	raw	st'pd	1	2	3	4	5	6	7	8	9	10	
Cold Water Extract %	7.83	5.45	6.10	8.46	11.36	13.40	15.40	15.89	16.37	16.68	16.68	17.44	16.83
Soluble N ..	228	187	217	250	396	432	465	472	469	469	480	490	443
Coagulable N ..	77	46	63	69	88	98	122	120	134	135	140	135	101
Coag. N % on N	4.12	2.46	3.39	3.69	4.71	5.25	6.53	7.34	7.18	7.23	7.50	7.23	5.41
P.S.N. ..	151	141	154	181	308	334	343	335	338	334	340	355	342
P.S.N. % on N	8.09	7.54	8.25	9.69	16.5	17.9	18.4	17.9	18.1	17.9	18.2	19.0	18.3
Formol-N ..	19.2	22.7	28.7	49.0	104	116	122	120	111	111	114	119	112
Formol-N % on N	1.03	1.21	1.54	2.62	5.57	6.21	6.53	6.43	5.94	5.94	6.10	6.37	6.00

It will be noticed that the balance between downgrade and upgrade processes was reached in the case of this malt about the 5th day, corresponding with other enzymic processes. Schild held that the fall in formol-nitrogen during the latter half of germination indicated that smaller quantities of polypeptides and amino-acids were being produced than were required for growth. It is not strictly correct to assume that the coagulable, permanently soluble and formol nitrogen respectively represent compounds of high, medium and low molecular complexity, but increase in the permanently soluble and formol nitrogen may be taken broadly to represent progressive simplification. The general conclusion from these and other published analyses is that protein cleavage during malting is far-reaching, since over 50% of the permanently soluble nitrogen produced is formol titratable. The breakdown is greatest, as a rule, between the 2nd and 5th days on the floor, the apparent standstill after this being attributed to formation of insoluble proteins in the acrospire, while there is a decrease of proteins in the endosperm.

(156) Soluble Nitrogen and Barley Variety.

The figures in Table 41 for permanently soluble and formol nitrogen would be considered low for normal English malts. These may give 25 to 30% of their total nitrogen as permanently

soluble nitrogen in a cold water extract, with correspondingly higher figures for the other fractions than those in the Table. The variety of the barley, its maturity and total nitrogen content all play a part in determining the permanently soluble and formol nitrogen, as well as the malting conditions which determine the higher figures for English in comparison with lager malts. Six-rowed barleys of Mediterranean type give a considerably lower percentage of permanently soluble on total nitrogen than two-rowed barleys. The figures in Table 41 are comparable with those given by an English-made Californian malt. Immaturity and high nitrogen content, which so often occur together, both lead to reduced percentages under comparable malting conditions.

The permanently soluble and formol nitrogen are more frequently determined in the laboratory hot mash than in extracts at 32° Fahr. The permanently soluble nitrogen in these worts represents not only that existing in the malt but also the further quantity produced by proteolysis during mashing, but the results obtained are reasonably comparable with those of the cold extracts. Both illustrate the effects of barley variety and total nitrogen content in a satisfactory manner. The permanently soluble nitrogen of English malts, as found by analysis of the extract wort, is usually between 34 and 40% of the total nitrogen, while that of Californian malts ranges between 28 and 32%. Varietal differences within these groups are comparatively small, but Thunæus and Schroderheim²² found quite marked differences in the soluble nitrogen of Swedish varieties. There is a striking difference in the relation of formol to permanently soluble nitrogen in cold and hot extracts. Most of the increase in permanently soluble nitrogen in the hot mash wort is due to more complex compounds, so that the percentage of formol-nitrogen in it is only about 25% compared with over 50% in the cold water extract.

It is rarely that the full proportion of soluble or permanently soluble nitrogen can be made available in high nitrogen malts, which almost always give a low percentage on total nitrogen, but it is difficult to dissociate the effects of immaturity from those due to nitrogen content and its influence on the relation between permanently soluble nitrogen and total nitrogen may override varietal differences. A prematurely ripened barley gives low values, while unusually high percentages are readily given by very mellow barleys and by many harvested in wet seasons.

(157) Conditions of Germination and Permanently Soluble Nitrogen.

Germination temperature appears to be the decisive factor in the production of permanently soluble nitrogen. Brown's

results suggested that proteolytic activity becomes more intense with rising temperature on the malting floor. This appears to be the case within the normal range of germination temperatures in cool malting, but not if a wider variation in temperature is considered. Schjerning²³ found that there was an optimum zone for proteolytic breakdown between 55° and 63° Fahr. More of the total nitrogen became soluble by the 4th day with a higher starting temperature of 68° Fahr., but it did not continue to increase as it did between 57° and 60°, and was considerably lower on the 7th day than with cool malting. The figures were 30.9% and 38.2% on the 4th day in a Congress mash with germination temperatures of 57° and 68° and 45.8% and 39.0% respectively on the 7th day. Other investigators have found that the P.S.N. remains practically constant at low temperatures after attaining a maximum on about the 6th day, but that there is a fall during the latter half of germination at higher temperatures with more energetic growth. The general result is that enzyme production is more active with a greater accumulation of soluble nitrogen in cool grown malts, because less is utilised by the more slowly growing embryo.

Very considerable variations in soluble nitrogen can be produced by differences in the amount of aeration. In the extreme case of a CO₂ rest, it is possible considerably to increase the soluble nitrogen and formol-nitrogen owing to inhibition of growth in an atmosphere of CO₂, while enzymic action continues. In floor malting, however, soluble nitrogen may be increased by excessive aeration.

TABLE 42.—EFFECTS OF TEMPERATURE IN EXPERIMENTAL MALTINGS

Days' growth		3	4	5	6	7	8	9
Soluble N % on total N ..	A	27.4	35.4	38.3	36.8	37.6	36.5	37.0
	B	31.2	33.4	35.5	34.2	31.9	—	—
	C	30.5	33.1	32.1	31.2	30.0	—	—
Formol-N % on total N ..	A	8.9	11.2	13.3	14.5	14.0	14.2	14.6
	B	10.3	10.5	10.7	11.1	10.8	—	—
	C	10.0	10.8	10.4	10.8	10.6	—	—
Extract % Plato on dry ..	A	75.8	78.4	79.2	79.4	79.7	79.6	79.7
	B	77.6	78.3	78.6	78.2	78.3	—	—
	C	77.9	78.3	78.5	78.2	78.2	—	—
1,000-corn wt. dry grm. (Barley 40.6 grm.) ..	A	39.6	39.2	38.7	38.2	37.9	37.7	37.5
	B	39.0	38.6	38.0	37.6	37.2	—	—
	C	38.9	38.3	37.7	37.2	37.0	—	—
Acid 100 ml., ml. N/10 NaOH to <i>p_H</i> 9.2 ..	A	13.2	15.6	16.1	15.5	15.6	15.5	15.7
	B	15.0	14.6	14.6	14.1	14.0	—	—
	C	14.4	14.3	14.1	14.1	14.0	—	—

The figures in Table 42 by Piratzky and Rehberg¹⁵ show analytical differences resulting from germination at different temperatures, Congress methods of analysis being used. The germination temperatures were (A) 55.4°–62.6° F., (B) 59°–68° F., and (C) 66.2°–71.6° F.

Hofman-Bang²⁴ found the greatest percentage of salt-soluble nitrogen in malts made at the lowest temperatures and in presence of CO₂ and suggested that barleys rich in this protein fraction may give such an increase that yeast may be over-nourished or protein deposits form in the beer. This might be an important point in the use of six-rowed barleys, which contain a comparatively low percentage of their nitrogen in salt-soluble form. He further suggested that more salt-soluble nitrogen may be permissible with strongly hopped beers on account of greater precipitation in the copper, and that some barleys with high nitrogen content may be so poor in this protein fraction that not only barley drying, but cold malting also are essential for brewing beers with full palate.

(158) Proteolysis on the Kiln.

The figures already given suggest that under normal conditions there is only very slight proteolysis during the kilning of pale malts. The case is, however, different in the kilning of dark aromatic malts, in which some increase in the quantity of the lower protein degradation products is desirable, and under conditions of "stewing" proteolysis may be excessive. Kolbach and Schild's⁹ experiments indicated that proteolysis on the kiln is less dependent on the moisture content of the malt than is the conversion of starch and may, under favourable conditions, occur to an extent approaching that which takes place in the mash tun. The experiments referred to were carried out under very artificial conditions and cannot exactly represent what happens on the kiln, but the figures in Table 43 indicate the possibilities of proteolysis when temperature and moisture conditions are simultaneously

TABLE 43.—INFLUENCE OF TEMPERATURE AND MOISTURE ON THE PERMANENTLY SOLUBLE NITROGEN OF MALT

Moisture in Green Malt %	Lowest temp. at which increase of P.S.N. occurred	Temperature of Maximum Increase	Maximum increase N per 100 grams Dry Malt
43	72° Fahr.	133°–136° Fahr.	300 mgms.
34	79° „	above 140° „	230 „
24	104° „	144°–151° „	150 „
15	122° „	151°–158° „	60 „

favourable. They refer to increase of permanently soluble nitrogen when green malt was kept for eight hours at the temperatures and moisture percentages stated.

MINERAL CONSTITUENTS OF MALT

(159) The Ash of Malt.

The figures given in Table 44 from analyses by Schönfeld²⁵ of the ash of a large number of Continental malts show the considerable variations which occur in its principal constituents.

TABLE 44.—ANALYSES OF THE ASH OF MALT

	Limit % on Dry Malt in the samples
Total ash	2.09 -2.55
Silica, SiO ₂	0.414-0.714
Total phosphoric acid, P ₂ O ₅	0.755-1.040
Soluble phosphoric acid, P ₂ O ₅	0.159-0.580
P ₂ O ₅ in alkali salts, K	0.068-0.309
P ₂ O ₅ in Ca and Mg salts.. .. .	0.031-0.075
Lime, CaO	0.117-0.178
Magnesia, MgO	0.167-0.309

The mineral matter of barley is largely combined with organic matter and liberated by enzymic action during malting in the manner indicated for the phosphates in the next paragraph. The salts are essential as yeast nutrients, the phosphates, potassium and magnesium being particularly important in this respect. Sulphates and small quantities of iron and other metals also occur in the ash. The remarkable similarity between the soluble mineral constituents of malt, and the most commonly used mineral yeast-nutrient solutions, is referred to in the chapter on wort composition. In addition, the phosphates are important in connection with the reaction and buffering of wort through reactions with the ions in the liquor.

(160) The Phosphates of Malt.

The changes in the phosphorus compounds in barley during malting may be considered in comparison with those of nitrogen. Phosphorus exists in barley almost entirely in combination with organic substances, in the form of phytin for example. Phytin is a magnesium-calcium compound of inositol phosphoric acid, inositol being a hexa-hydroxy-cyclo-hexane with the same empirical formula as a carbohydrate and believed to be one of the con-

stituents of Bios which is essential for yeast growth. During malting enzymes referred to as phytase or phosphatases act on the organic phosphorus compounds and convert about 20% of the phosphorus into the form of inorganic phosphates, mainly potassium phosphates. The figures in Table 45 were given by Prior for changes in the phosphoric acid combinations.

TABLE 45.—CHANGES IN PHOSPHORIC ACID DURING MALTING

	Barley	Steeped Barley	Days' germination			
			2	4	6	8
Total P_2O_5 ..	0.968	0.898	0.882	1.038	0.923	0.941
Primary phosphate ..	0.232	0.214	0.250	0.379	0.369	0.403
Do. as % of total P_2O_5	23.4	23.9	29.5	30.5	39.9	42.8

(161) The Acidity of Malt.

The acidity of malt has a considerable influence on its brewing quality. It appears small when expressed as lactic acid, but variations have an influence on enzymic conversions in the mash tun. Its development during malting is largely due to the conversion of organic phosphorus compounds to inorganic acid phosphates, which follows a course very similar to that of other enzymic changes, as shown in Table 46 (Kolbach and Antelmann²⁶). Organic acids are formed as intermediate products in the oxidation of carbohydrates and it is possible that a small proportion of lactic acid is produced. The lactic acid found in the extract wort of English malt averages about .003% of the malt, or between 1/20 and 1/25 of its total acidity.

TABLE 46.—ACIDITY CHANGES DURING MALTING
(REFERRED TO 100 GRAMS DRY MATTER)

	ml. alkali or acid to		Buffering p_H 4.27-7.07	p_H
	p_H 7.07	p_H 4.27		
Barley	22.0	41.6	63.6	6.05
Steeped Barley	20.2	36.4	56.6	6.10
Germination 2 days ..	23.0	43.6	65.8	6.18
4 " ..	25.7	45.7	71.4	6.29
7 " ..	28.4	46.8	75.2	6.28
9 " ..	29.2	47.3	76.5	6.21
Kiln, upper	29.9	49.8	79.7	6.29
lower	31.3	40.0	71.3	5.94
Congress wort	41.6	45.6	87.2	5.83

(162) Formation of Buffers during Malting.

It is striking that, despite the increase of titratable acidity, shown in Table 46, the p_H of cold water extracts actually increases. This is attributed to rise in the buffer content of malt during germination. The changes in buffer content of an English malt are shown in Table 47 from analyses by Hopkins and Kelly.²⁷

TABLE 47.—ELECTROMETRIC TITRATIONS OF COLD WATER EXTRACTS OF MALT (ML. N/10 H_2SO_4 OR NaOH TO CHANGE THE p_H OF THE EXTRACT OF 50 CORNS BY 1.0)

Sample	p_H	Buffer ratios over range of p_H		
		7.0-5.7	5.7-4.3	4.3-3.7
Original Norfolk Barley	5.83	0.35	0.34	0.42
As cast from steep	5.17	0.13	0.16	0.23
2 days on floor	5.17	0.15	0.16	0.23
4 " "	5.65	0.36	0.22	0.36
8 " "	5.90	0.45	0.26	0.39
10 " "	5.93	0.43	0.26	0.39
12 " "	6.03	0.48	0.33	0.46
Shortly after loading on kiln ..	5.93	0.51	0.36	0.49
Hand dry stage	5.80	0.60	0.37	0.53
Finished Malt	5.66	0.58	0.35	0.46

The period of quiescence during the first two days, followed by rapid production of buffers, resembles the course of events with other enzymes. The figures are from electrometric titrations with N/10 acid or alkali and expressed as buffer ratios, according to Van Laer's suggestion, or as the number of ml. of N/10 acid or alkali required to change the p_H of 25 ml. of the cold water extract, representing 50 corns, by 1.0. The buffer ratios, while only of relative value, serve to indicate the quantities of the respective types of buffers extracted from minced and triturerated corns at 70° F. They were calculated over the following p_H ranges:—

p_H 7.0-5.7, mainly influenced by inorganic phosphates.
 p_H 5.7-4.3, " " amino-acids and peptones.
 p_H 4.3-3.7, " " " "

These figures show that about half the buffers of barley are removed in the steep, probably extracted from parts of the corn outside the testa. These are relatively alkaline and include some phosphates, hence the p_H falls. During active germination the soluble phosphates increase by two or two and a half times, as indicated by the buffer ratios in the phosphate zone. The buffering in the amino-acid zone increases at the same time by about 150%, while the p_H value rises.

It is interesting to note that the p_H value of steeped barley approximates to the optimum for the enzymes which produce phosphates in malt. Lüers found an optimum at p_H 5.2 for phytase and Adler an optimum at p_H 5.4 for phosphatase. The rapid change to p_H 5.8-6.0 approximates to the optimum of p_H 5.5-6.0 found by Ohlsson for α -amylase at 100° F. The activation of α -amylase during the early days of germination, liberation of inorganic phosphates, formation of amino-nitrogen, and the sudden rise of p_H are probably all closely related.

OTHER MALT CONSTITUENTS

(163) Changes in the Fat of Barley during Malting.

It is possible that some of the increase in the acid content of malt may be due to the breakdown of fats by lipase. The figures by Sedlmeyer²⁸ show some of the changes in the fat of barley, of which the greater quantity remains in the grains after mashing.

TABLE 48.—CHANGES IN THE FAT OF BARLEY DURING MALTING
(PER CENT. ON DRY SUBSTANCE)

	Barley	Steeped Barley	Green Malt
Total Fat	2.07	1.97	1.41
Unsaponifiable Fat ..	0.111	0.104	0.105
(a) Stearine	0.065	0.054	0.052
(b) Non-stearine ..	0.046	0.048	0.052
Lecithin	0.66	0.63	0.64

(164) The Tannin of Malt.

Comparatively little is known about the tannin of malt, but the quantity existing in the husks would appear to be of some importance in relation to precipitation of proteins in the copper. Hartong²⁹ found that an unhopped 12% wort contained 0.0111% of tannin, which would mean nearly 1% in the malt. This is perhaps an over-estimate, the figures suggested in Table 27 being perhaps more usual, but its existence must be of greater moment in lager brewing than in malts mashed by infusion methods, since more would be extracted by boiling the decoction mash. In addition the amount of tannin derived from hops is less in lager worts, increasing the relative importance of the malt tannin. Hartong found only 0.0080% derived from the hops in a Pilsen wort. The flavour of the tannin is acrid and with resinous substances in the husks accounts for the objection to husky six-rowed malts in lager brewing. On the other hand, complete absence of these flavouring substances has been stated to give beer lacking in flavour.

(165) Influence of Husks on Wort and Beer.

The uncertainty in regard to malt tannin is illustrated by the results of brewings by Rehberg³⁰ of Pilsen type beer with grist from which the husks had been separated. The beers were very pale in comparison with those brewed with the husks, the increased colour of the latter being attributed to reddish-brown oxidation products of husk tannin formed during mashing and boiling and to reactions with iron. The worts without husks were brighter than the controls. A notable point was that the husks were found to yield considerable quantities of buffer substances to the wort, mainly phosphates liberated from phytin, but they did not affect the p_H of the wort, though the buffers lessened the fall during fermentation. The milder flavour of the beers without husks was in this case considered advantageous. Husk extracts boiled with wort from de-husked malt did not increase the amount of nitrogen coagulated.

(166) Summary.

The most important constituents of malt are the starch, on which the extract mainly depends, the soluble carbohydrates or sugars, which also contribute to the extract, the proteins and their degradation products, on which the quality of the malt and character of the beer depend to a very considerable extent, hemicelluloses, which, in so far as they are converted to soluble pentosans, contribute to the colloidal properties of beer, and the mineral matter, consisting mainly of potassium phosphates, which react with liquor salts and help to determine the reaction of the mash and buffering of wort. They also, with calcium and magnesium, provide essential yeast nutrients. Apart from these chemical constituents there are the physiological agents of their breakdown, the enzymes, with bios and vitamins, which are dealt with in a later chapter.

The development of soluble products of enzyme activity during germination usually reaches a maximum about the 5th or 6th day on the floor, corresponding with the greatest attainment of diastatic activity in the malt, though later changes may be produced by sprinkling and the consequent stimulation of germination. There may also be quite considerable enzymic changes on the kiln up to a temperature of 140° Fahr., if the moisture content is sufficiently high or conditions referred to as stewing exist. These cause an increase in the cold water extract. There may also be a small increase in proteolysis if the conditions are favourable, but the increase in permanently soluble nitrogen is very small in normally-made malts. All enzymic activity ceases on the

kiln at 176°, but important changes in chemical composition, influencing the flavour and colour of the malt, then supervene.

The very comprehensive set of analyses by Piratzky³¹ in Table 49 provides an excellent summary of the changes in malt composition during germination and of the differences in analyses of under-modified and fully-modified malts. The following points may be noticed :

(1) Influence of lower germination temperature on proteolysis and maltose in the laboratory wort. It produces more soluble nitrogen, a greater percentage of formol-nitrogen and more apparent maltose.

(2) Increasing extract with germination and decreasing difference between total extract and laboratory extract with coarse ground malt. The figures in the column headed Graf refer to extracts determined by Graf's method for barley with a diastatic extract.

(3) Increase of soluble nitrogen throughout germination. Increase of formol-nitrogen up to about the 5th day.

(4) Decrease of viscosity of laboratory wort with increasing modification. The figures are based on flow times from a burette at 20° C., but are not in C.G.S. units.

(5) Reduction in the quantity of precipitate from laboratory wort by trichlor-acetic acid in cold grown malt, but gradual increase with warm grown malt. Increase in the protein content of this precipitate with increasing modification.

(6) Changes in the nitrogen content of malt during germination.

TABLE 49.—CHANGES IN MALT DURING GERMINATION

Dys.	N%	Extract %		Sol. N % of N		Congress wort		ρ_H	Viscosity water = 1000	Boiled 5 hrs.		Trichlor-acetic acid ppt.	
		Graf	Coarse	Graf	Coarse	Mal- tose %	Formol N % sol N			pptd. mg.	protein % in ppt.	mg.	protein %
GERMINATION TEMPERATURE 55°-59° Fahr.													
0	1.82	77.8	—	15.9	—	—	—	—	—	—	—	—	—
1	1.86	78.4	—	17.2	—	—	—	—	—	—	—	—	—
2	1.83	78.3	—	19.8	—	—	—	—	—	—	—	—	—
3	1.81	80.2	73.1	32.3	26.2	63.0	17.9	6.09	1340	58.0	33.1	82.6	21.9
4	1.76	80.7	75.7	36.7	33.5	64.4	15.9	5.97	1202	53.4	47.5	71.4	38.8
5	1.79	80.1	77.6	38.9	34.3	63.4	19.3	5.96	1121	47.4	64.4	65.1	45.0
7	1.80	80.7	78.0	40.6	35.4	66.1	20.1	5.95	1081	36.9	96.3	57.3	59.4
9	1.79	80.8	78.3	41.9	37.0	68.3	19.4	5.95	1068	39.1	96.3	57.9	63.7
11	1.79	80.9	78.5	41.7	39.6	70.2	20.1	5.93	1062	37.5	90.7	58.9	56.9
16	1.85	80.1	78.2	45.5	38.6	71.1	19.9	5.92	1063	37.8	90.0	57.5	65.6
GERMINATION TEMPERATURE 64°-70° Fahr.													
0	1.82	77.8	—	15.9	—	—	—	—	—	—	—	—	—
1	1.86	77.4	—	16.2	—	—	—	—	—	—	—	—	—
2	1.90	78.8	—	17.1	—	—	—	—	—	—	—	—	—
3	1.83	79.2	73.0	30.9	25.9	62.1	17.4	6.19	1316	67.1	35.0	46.7	37.5
4	1.84	79.4	76.5	33.9	29.4	69.4	16.7	6.10	1149	50.3	52.5	45.4	57.5
5	1.70	79.4	76.6	36.0	27.3	66.1	17.4	6.04	1098	43.0	66.9	51.8	61.2
7	1.79	78.7	76.4	33.0	28.3	65.2	18.2	6.04	1082	35.5	83.7	54.4	54.9
8	1.79	79.8	77.2	33.7	30.5	68.7	17.6	5.99	1069	34.7	88.8	53.0	58.8
UNDER-MODIFIED AND WELL MODIFIED MALTS													
8	1.84	80.7	76.5	26.1	22.0	62.8	15.5	5.94	1139	30.3	63.7	41.6	46.9
11	1.84	80.3	79.7	33.7	33.0	65.0	20.2	5.98	1073	38.1	81.9	51.1	66.2

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CHAPTER X

COMMERCIAL ANALYSIS OF MALT

(167) Types of Malt.

Ordinary or "white" malts may be divided into a number of types according to the variety of the barley from which they were made and the purpose for which they are suitable. Barley variety takes a prominent place among the characters on which the utility of malt depends, but the main criteria of quality apply to every variety. Structural differences, in which the quantity of husk is an important factor, place malts from two- and six-rowed barleys in very distinct categories. A proportion of six-rowed malt improves the drainage in an infusion mash, but the danger of extraction from the husks of substances giving a straw-like flavour may more than counterbalance any possible advantage in this direction in a decoction mash. Malts from Mediterranean and Manchuria barleys again mark out two distinct types. Decided preferences for one or the other are shown by different brewers. This is more a question of composition, enzymic and germinative activity than structure. The high-nitrogen Manchuria malts are particularly suitable for use with a high proportion of unmalted cereals, their great enzymic activity being appreciated in American breweries. On the other hand malts from barleys of the Mediterranean type are preferred by brewers in Great Britain.

The difference between ale and lager malts depends largely on the kilning processes but in each group the drying and curing temperatures and the manner of applying them are varied to produce pale and dark types. These are referred to broadly as pale ale and mild ale malts or Pilsen and Munich malts respectively. Drying and curing extending over 3 to 5 days, after typically fuller modification, gives pale ale malts characteristics of flavour lacking in the much paler lager malts of Pilsen type, which are usually dried at lower temperatures on double-floor kilns, allowing 24 or only 12 hours on each floor. The differences are not so great in the malts intended for mild ales and dark lagers, though the shorter, two-floor kilning and heaping, with advanced temperatures, while the moisture content is compara-

tively high, gives malts of Munich type a distinctive character not found in the majority of English dark malts.

Although colour is an important type distinction, differences in barley composition are taken into account when making up the malts. These are largely connected with the nitrogen content. The better qualities or lower nitrogen barleys are generally, but not always, made up into pale malts. The medium and lower grades, with higher nitrogen content, are usually made up into mild ale or dark malts, the aromatic flavour and colour of the malts depending on reactions during curing in which nitrogenous substances play an essential part.

Grades in each type of malt are marked by differences in extract, colour and enzymic activity, all of which can be related to the nitrogen content. Judicious selection and blending in grists for different kinds of beer goes a long way towards production of the character desired in the beers. Pale dried malts are not restricted to pale beers and they are largely used with a comparatively high proportion of roasted malt or barley in stouts. A darker malt, with its attendant fuller flavour, may on the other hand be used for pale ales in which a moderate proportion of grits or flakes is employed.

(168) Physical Character of Malts.

Malts are judged in a manner similar to that described for the hand examination of barley, but any gross defects in the latter should have decided their rejection, so that faults are less likely to be found in malts. Weather stain becomes less noticeable by malting and in some cases may be almost or entirely eliminated. In many cases the stain, which reduced the barley grade, has no effect on the brewing value of the malt and is accompanied by greater mellowness, actually producing a better malt than that from apparently superior barleys, so that malts after a damp season are not infrequently better than those of a dry season. It is, however, difficult to detect the effects on malt of unsoundness in the barley, for which reason it is safest to accept the more critical examination of barley. The advantage of soundness which imported six-rowed barleys have over English two-rowed in a wet season is generally a decisive factor in blending a proportion of malt from the former in ale grists. There can be no doubt that physiological changes in the barley associated with the description "unsoundness" result in lack of stability in beer, but at present it does not seem possible to give any clear explanation of this. It is for this reason that empirical skill in detecting it in barley is so valuable and still remains an essential safeguard against trouble in the brewery. It is well to

err on the side of safety, if it ever can be an error to be on the safe side, and make certain that malt is made from sound barley. There are no doubt many barleys and malts of defective appearance which could be used with perfect safety, but, in the absence of any scientific means of discrimination, it is well to be cautious in their use.

A great danger comes from bulks of malt made up from barley containing a proportion of unripe or undeveloped corns, in which it is impossible to expect even growth and modification. Difficulties in fermentation, brilliancy and stability of beer are to be looked for when such malt is used. The sinker test will often pick these corns out with the dead ones and is very helpful as a rough guide to the regularity and quality of malt. In addition malt should always be bitten down to test for flavour and hard corns and rejected if many of the latter occur in it or if any defects in flavour due to mustiness or lack of curing appropriate to its class are detected. Very few damaged or mould-affected corns should occur in high class malts but a small number may be found in the lower grades, though rarely in sufficient quantity to affect the flavour of the beer.

(169) Objects of Malt Analysis.

Malt analysis is used both as a means for investigating the quality of malt and for control of commercial and brewery operations. A few simple determinations may cover all that is required for many control purposes but the tendency is to extend these in directions which, it is believed, afford criteria of quality. This is particularly the case in connection with the control of malting operations or in respect of malt purchases. In all cases physical examination of the malt must be regarded as essential and in skilful hands it may, when combined with determinations of moisture, extract, colour, cold water extract and diastatic activity, provide all the information required for valuation of the malt. Analysis should, however, be capable of eliminating the uncertainty of physical tests and be able to characterise malt so definitely as to prove whether it is the best that could have been obtained from the barley, with due consideration of the purpose for which it is intended. The analysis should give all the information required to decide on the suitability of the malt for the beer required, and for the brewing methods adopted. It should also indicate the probable behaviour of wort and beer made from the malt under existing conditions.

(170) Standard Methods of Analysis.

Standard methods of malt analysis have been available for some

years for ordinary commercial purposes. They owe their origin to realisation of the fact that concordant results for such determinations as were and are still customary could only be secured by use of identical technique in every laboratory. The methods of analysis involved are entirely empirical but the conditions of experiment are so explicitly laid down in the standard methods that the risks of disagreement are reduced to a minimum, with ordinary manipulative skill. The prescribed determinations are intended to be simple, rapid and reproducible. They give quantitative expressions for some of the most important characters of malt but do not claim to give sufficient information on its composition or on that of its extract for complete appraisalment of brewing quality.

Three sets of standard methods of analysis have been published. These are the Standard Methods of Malt Analysis of the Institute of Brewing,¹ London, 1933, which is a revision of earlier compilations of 1906 and 1922; the standard methods of the Salzburg Congress of 1929,² which came into force on January 1st, 1930, displacing those of the previous Bonn Convention, and the Official Methods for Analysis of Malt published by the Malt Analysis Standardisation Committee, Chicago, 1935. The first is more particularly applicable to malts used in top-fermentation brewing, the second is generally accepted by European and other lager brewers. These have proved their value over a number of years and the third will no doubt be found equally useful under American brewing conditions. The analytical determinations included in the standard methods are detailed in Table 50, with the main points in which they differ.

TABLE 50.—COMMERCIAL ANALYTICAL DETERMINATIONS FOR MALT

Determination	Institute of Brewing	Salzburg Congress	American Committee
Moisture %	Boiling Water Oven	At 104°–105° C.	At 103°–104° C.
Extract	Brewers' lb. or degrees per qtr. Coarse grist	Per cent. Plato Fine grist	Per cent. Plato Fine grist
Colour	Tintometer, 52 scale in 1-inch cell	N/10 iodine or Brand	Tintometer, 52 scale in $\frac{1}{2}$ -inch cell
Cold water extract	Per cent. on malt	—	—
Diastatic activity	Lintner value	—	Lintner value
Saccharification	—	Time in minutes	Time in minutes
Appearance of wort	—	Clarity	Clarity

The American Committee has based its methods for moisture and extract determination on those of the German compilation and has followed the English in adopting Lintner's method for diastatic activity and the Lovibond Tintometer for colour estimations.

The Salzburg Congress prescribed a form of report in which extract on moisture-free malt, extract on coarsely ground malt, odour of the mash and speed of filtration, together with a report on mechanical examination including hectolitre weight, thousand-corn weight and character of the endosperm may be given in addition if requested by the client. The speed of conversion to iodine normality, the odour of the mash, the speed of filtration are also reported in the American methods, together, if desired, with the extract on coarsely ground malt "as is" and on dry basis. These details are not required by the English Standard methods and no determination of cold water extract is laid down by the other two. The Congress methods do not prescribe a determination of diastatic activity but the Windisch-Kolbach and Lintner methods are frequently used.

The results of analyses by these methods are often applied quite literally to the appreciation of malt quality, which is accepted as satisfactory if each determination falls within a range that experience has shown characterises good malt of its type. This may lead to errors of interpretation, as will be illustrated in a later chapter by analyses of malts in which additional information has been obtained by analytical methods not included in the standard determinations. Nevertheless the latter all have important implications which must be considered together and in the light of any information available on the type of barley used, the method of malting and the use to which the malt is to be put.

(171) Sampling.

All three compilations lay the utmost stress on the necessity for representative samples of bulks. This is a point that cannot be over-emphasised as bulks of malt are not homogeneous and it is not at all an easy matter to get identical duplicate samples. A number of samples from various parts of the bulk or from 10% of the total number of sacks must be thoroughly mixed and duplicate small samples be taken from the large sample. It is particularly difficult to get representative samples from a kiln, in which case samples should be taken from various places, by different people if possible to avoid individual selection. Division of the large sample into duplicates is most easily accomplished in a sample-dividing apparatus, which may consist of a

rectangular metal box divided by a number of transverse partitions into little hoppers delivering alternately to either side. A large sample poured into this as evenly as possible will be divided into two equal parts and delivered through the spouts of the hoppers on either side. One of these can be passed through

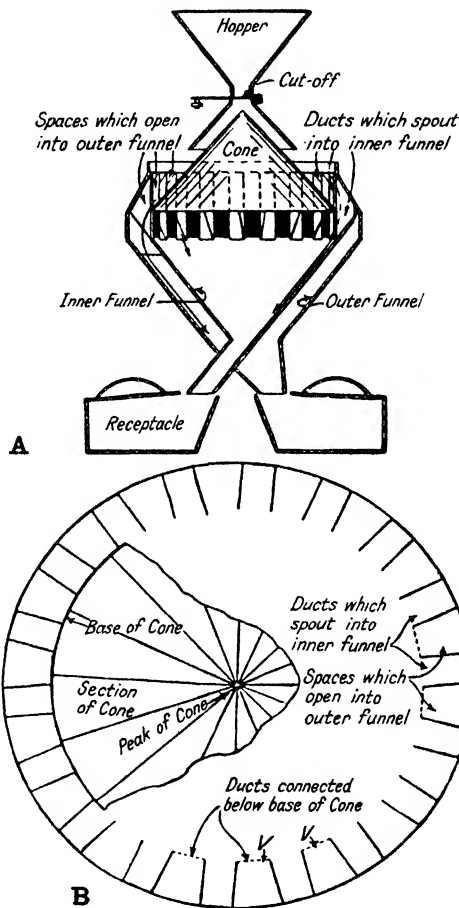


FIG. 37

SAMPLE DIVIDER. (A) VERTICAL CROSS SECTION, SHOWING PATHS TAKEN BY THE MALT IN PASSING FROM THE HOPPERS TO THE CONTAINERS; (B) CROSS SECTION OF THE BASE OF THE CONE

again and further subdivided until two analysis samples of the required size are obtained. The process is very rapid so that absorption of moisture is reduced to a minimum. The Boerner Sampler, constructed on this principle, Fig. 37, is described in the American compilation. All samples must then be placed in air-tight containers, one for analysis and its duplicate as a reserve. A sample divider should find a place in all laboratories in which

analyses of malt and barley are made, as it is difficult otherwise to obtain representative portions even from a comparatively small sample.

(172) Moisture Content.

The determination of moisture might appear to be one of the simplest of analytical operations but actually this is not so in the cases of barley and malt on account of the difficulty in distinguishing between "moisture" and combined water, which may be liberated by decomposition of the various constituents of the grain. The figures given in Table 51 will show the variable results that may be obtained by different analytical methods. They were obtained by Coleman and Snider,³ in a comparative study of these methods in which they used the vacuum desiccator as the standard of reference, because no decomposition or caramelisation occurs when the sample is kept under a pressure reduced below 10 mm. of mercury over anhydrous P_2O_5 . They found that the Brown-Duvcl method did not consistently determine the moisture of malt with accuracy but obtained good results by means of a modified Bidwell-Stirling distillation method. They state that the dielectric method has not been developed with sufficient accuracy for all types of malt and moisture percentages, while the conductivity type of electrical moisture-testing apparatus as now constructed is not suitable for malt. These authors do not appear to have tested a boiling water oven through which a current of dry air is drawn but the note added is probably in agreement with their results.

TABLE 51.—COMPARISON OF METHODS OF MOISTURE DETERMINATION

Method	Temp. C.	Time	Comparison with standard
Air oven	130°	$\frac{1}{2}$ hr.	0.63% higher
Vacuum oven, 25 mm. press.	100°	5 hrs.	0.25% higher
Carter-Simon method ..	132.5%		0.5% higher
Vacuum oven, 25 mm. press.	70°	18 hrs.	0.1% lower
Air oven	103°–104°	3 hrs.	practically equiv.
Boiling water oven ..	98°	5 hr.	0.26% lower
Do. with dry air current ..	98°	3 hr.	practically equiv.

The importance of standardisation of moisture determinations is obvious, as on it depends the exact comparison of extract determinations but experiments showed that a daily variance

of approximately 0.2% was to be expected with the air oven at 103°–104° and this, combined with the sample variance, indicates that closer agreements than 0.3% with different portions of the same lot of malt cannot be expected. A similar tolerance must be allowed with the boiling water oven. It will be noted that the latter has been adopted as the standard for moisture determinations in England, while the Congress and American methods stipulate air ovens which give, according to these experiments, 0.26% more "moisture" from the same sample.

The moisture content of malt is considered to have a most important influence on its behaviour. Very rigid limits are set by brewers who use an infusion mashing system. Generally this is 3% and various defects, such as instability of beer, clarification difficulties and defective flavour are attributed to malts containing more than this percentage. Although the accumulated evidence of experience is so strongly against using malt in an infusion mash with a higher percentage of moisture, there is no very definite proof that the moisture content is in itself the cause of these difficulties or that any change in malt composition occurs during storage for a reasonable time when the moisture materially exceeds 3%. Successful use of re-dried malt is indeed against the usual belief and it is difficult to believe that any enzymic or other deleterious changes occur through short contact with moisture in excess of this in transit or during storage in the warm, moist atmosphere of the brewery malt room, where condensation on cold malt causes a rapid increase.

There are practical objections of another order to using malt with over the normal moisture content of 2 or 2½%. There is an apparent loss of extract if it is weighed at the mill, and there may be an actual loss through defective grinding. A high moisture content causes variation in the composition of the wort if the malt is mashed at the normal temperature, but the change does not appear to be anything more serious than can be rectified by raising the initial heat of the mash. It arises from the fact that the heat generated when dry malt is mashed is considerably greater than when the malt is slack. If two malts, one containing 2% and the other 6% of moisture are mashed at the same rate with water at 150° F., the initial heat of the mash with the slack malt would be about 4° lower than that with the other. This results in rather different wort composition, more maltose would be found in the wort from the slack malt. The difference is sufficient to be detected by the polarimeter when a malt containing 1 or 2% more moisture than usual is inadvertently used in a brewery where the $[\alpha]_D$ of every wort is determined as a matter of routine.

This difference in initial heat does not arise with the low mashing temperatures employed in decoction mashing. Lager brewers prefer that the malt should contain about 4 or $4\frac{1}{2}\%$ of moisture, in the belief that the colloidal state of its constituents does not become stabilised until the malt has been stored for some months with at least that quantity of moisture. The usual moisture content for lager malts when used varies between 4 and 7%. This has an advantage in reducing the production of flour in the mill with the less fully modified malts.

(173) Extract of Malt.

By extract is understood the quantity of solid matter extracted from malt in relation with the weight mashed under specified conditions. The extract yielded by malt is its most important economic property but not necessarily any criterion of its brewing quality, which depends on the composition and colloidal state of the extracted matter. If barley is bought the extract should be calculated back to raw barley steeped in order to find the cost of each unit. In this connection it should be noted that extract increases up to a point during germination but there is at the same time an increase in malting loss, so that even with an increasing extract on malt there may be a decrease when it is calculated back to barley steeped and sometimes there is an actual decrease in the extract on malt with protracted germination. Examples of the extract obtained from different types of malt are given in Chapter XII and, although the six-rowed malts nearly always give considerably less extract than two-rowed, imported six-rowed barleys not infrequently give a higher extract on raw barley than English on account of their lower moisture content and malting loss.

There are several ways of determining and expressing the extract of malt. It is not feasible to evaporate wort to dryness and weigh the dissolved solid matter on account of the grave risk of partial decomposition, nor would this in any case be practicable as a rapid method of analysis. Two alternatives present themselves, the first of which is adopted in the Institute of Brewing standard methods of analysis and the second in the Congress methods. These are :

- (1) Use the specific gravity of the wort as an expression for the extract on the assumption that it bears a constant relation to the concentration of solid matter in the wort.

- (2) Calculate the percentage of solid matter in the wort from tables constructed to give the relation between specific gravity and concentration, and express it as a percentage of the malt used.

Use of the specific gravity of wort as a measure of the extract of the malt from which it was made, necessarily assumes that a specified volume of the wort is obtained from a given weight of the malt. The weight and volume conventionally used in Great Britain are the quarter or 336 lb. of malt and the barrel or 36 Imperial gallons of wort. The extract of the malt is then expressed as degrees of gravity per quarter or as brewers' pounds per quarter, colloquially abbreviated to degrees or pounds per quarter. Pounds per quarter is the more usual mode of expression but many brewers adopt degrees per quarter and so avoid the use of two methods for expressing gravity.

An explanation of these units, degrees of gravity and brewers' pounds, together with per cent. extract Balling and Plato, is given in Sections 239-242. Since degrees of gravity are specific gravity - 1000, the specific gravity of water being taken as 1000, and brewers' pounds represent excess weight over 360 lb., the weight of a barrel of water,

$$\text{Extract in brewers' pounds} = \text{Extract in degrees} \times 0.36.$$

In the Institute of Brewing standard method of analysis 50 grams of malt are mashed for 1 hour with 360 ml. of water at 150° Fahr. and the volume of the mash ultimately made up to 515 ml., under the assumption that the grains occupy a volume averaging 15 ml. The relation between malt and wort is thus assumed to be 50 grams to 500 ml. or a concentration of 10%. The specific gravity of this wort is taken at 60° Fahr. and that of a barrel of wort obtained from 336 lb. of the malt calculated from it, on the assumption that specific gravity and concentration are proportional. The extract per quarter of malt is thus given by

$$\text{Extract (degrees)} = \frac{(\text{sp.gr.} - 1000) \times 10 \times 336}{360}$$

$$\begin{aligned} \text{Extract (brewers' pounds)} &= \frac{(\text{sp.gr.} - 1000) \times 10 \times 336 \times 0.36}{360} \\ &= (\text{sp. gr.} - 1000) \times 3.36 \end{aligned}$$

Percentage extract, as adopted in the Congress analysis' means grams of dry wort solids obtained from 100 grams of malt. It is calculated from the specific gravity of the wort obtained in the specified manner by reference to tables which give the number of grams of cane sugar in 100 grams of the wort corresponding with its specific gravity. The tables used are those of Plato, which have superseded the older and less accurate Balling tables.

It is found by mashing 50 grams of malt with 200 ml. of water at 45° C. for half an hour, after which 100 ml. of water at 70° C. is added and the temperature of the mash slowly raised to 70° C. After a further stand of one hour it is cooled and its weight made up to 450 grams. The mash so obtained is assumed to contain $400 + \frac{1}{2}w$ grams of wort, w being the percentage of moisture in the malt. The specific gravity of the filtered wort is taken at 20° C. and its extract, or the number of grams of dry solids in 100 grams, ascertained by reference to the Plato tables. The extract of the malt is then calculated from

$$\text{Extract (\% Plato)} \quad \dots \quad \frac{P(800 + w)}{100 - P}$$

in which P is the extract % which according to the Plato tables corresponds with the specific gravity of the wort and w is the moisture content of the malt.

This formula and that for calculating the extract according to the Institute of Brewing method give the extract of malt with the moisture percentage existing in it, or as sometimes described, "as is" or "air dry." The extract on dry or moisture-free malt is calculated in either case by the following formula, in which E is the extract in malt and w its moisture content per cent.

$$\text{Extract, dry malt} \quad \dots \quad \frac{E \times 100}{100 - w}$$

It will be noticed that both methods of analysis are conventional. Neither of them accurately expresses the extract in the terms stated. The assumption of 15 ml. for the volume of the grains in the Institute of Brewing method is in excess of the truth for English malts, thus reducing the extract found, and lower than the true volume for husky six-rowed malts, giving too high an extract. The grains from two-rowed malts may occupy about 12 ml. and those of six-rowed malts about 17 ml.

The accuracy of the Congress method, which may appear at first sight to be more precise, is also seriously questioned on account of the use of cane sugar tables, with a solution divisor about 0.1 lower than that appropriate to wort solids, and also because water supposed to be in the wort is absorbed by the grains or used in the chemical reaction of hydrolysis of starch. Scientific accuracy is not, however, claimed for these methods. They, like all the other determinations prescribed in the standard methods of analysis, are essentially for commercial use and

their value depends on the closeness with which the results correspond with those obtained in the brewery under normal and satisfactory mashing conditions. Judged from this point of view, they are remarkably accurate. It is usual to get about 1% less extract in the brewery but frequently the agreement is complete and in many cases the brewery succeeds in obtaining a higher extract than the laboratory. The cause of greater deficits than about 1% or 1 lb. can usually be traced to technical defects in the malt mill or mash.

By whatever method the extract of malt is determined, it is essential that the extraction be carried out under precisely standardised conditions. The method of grinding is of particular importance. The Institute of Brewing specifies a Seck or Boby mill set with a roller separation of 0.5 mm. A finely ground grist is specified in the Congress and American methods, the grist being checked by standard screens. No flour must be lost in the mill, while all mashing conditions are strictly laid down.

(174) Colour.

Colour is such an important factor in the customers' appreciation of beer, that a good deal of research has been devoted to the elaboration of methods by which it could be accurately measured and recorded. Methods based on colour standards are subject to personal error but all attempts to replace them by more accurate scientific methods have so far failed to attain their object in a manner sufficiently simple to comply with the requirements of routine control. The colour of a substance depends on its specific light absorption and in such liquids as wort and beer there is selective absorption, with specific absorption coefficients for each wave-length. The result of this selective absorption is the colour as appreciated by the eye. The newer scientific methods of determining it are based on measuring the absorption, which can be directly related to the colour. Photo-electric cells, by which incident light is directly transformed into measurable currents, and the Pulfrich Photometer can both be used for this purpose.

Such exactitude as is aimed at in objective measurements with scientific instruments is hardly necessary for determination of the colour of wort or beer, for which direct comparison with standard solutions or coloured glasses is sufficiently accurate, given normal eyesight and a constant light source. Measurements in daylight are always subject to errors through variation in intensity and colour of the light, a point which the American Standard method has provided against by prescribing a standard light source. The utility of colour determinations of malt de-

depends on the possibility of comparing them with the colour of the finished beer. The relation varies to a considerable extent in different breweries, since it depends very much on the mashing liquor, method of boiling, oxidation, hops and other factors of this kind. Each brewer must consequently study this point under his own conditions and fix his own standards of malt colour for pale or dark beers.

The wort prepared for extract determination is used in all the standard methods for determining the colour of malt. The Lovibond Tintometer is prescribed by the English and American Committees, comparison being made between the wort in 1-in. and $\frac{1}{2}$ -in. cells, respectively, and glasses of the 52 series. A decinormal solution of iodine is used as standard in the Congress analyses, the colour of the wort being denoted by the number of ml. which must be added to 100 ml. of water to produce a match with the wort. Since iodine solutions fade rapidly they are frequently replaced by standard dye solutions based on them. These are made at the Scientific Stations from the following dyes,

Victoria yellow	..	16
Patent blue	..	1
Fast brown	..	2.5
Bordeaux	..	4

1.15 gram of these dyes, well mixed, dissolved in 1 litre of 20% alcohol gives a colour very close to that of N/10 iodine solution. The colour of the solution is not permanent and the standards must be replaced from time to time. They form what is known as the Brand Scale.

Limits must necessarily be set to the colour of a malt on account of the preference of customers for pale or dark beers and the criticism that may follow any deviation from regularity. Other factors, such as the increase produced in the copper, come into play in deciding the colour of beer but the colour of the malt is of first importance. Its actual value must be found by experience, thus if malt with a colour of 5.0 could be used safely in a brewery employing gypseous water it might be necessary for another, with carbonate liquor, to set the limit at 4.0 for beer of the same gravity and colour. The upper limit for malt colour naturally rises with decreasing beer gravity but not proportionally on account of the increases and decreases which occur during boiling and fermentation, but if 4.0 or 5.0 are suitable for beers of 1055 gravity, about 6.0 to 7.0 would generally be required to give a similar colour in 1040 beer. Deficiencies in colour are readily made up by use of caramel or coloured malts but with the possibility of some modification in the flavour

of the beer. As a rule, but not always, the colour of a malt is a guide to its flavour and diastatic activity and the requirements in these respects must be considered together, low colour with dry flavour and high diastatic activity against high colour, fuller, sweeter flavour and low diastatic activity. Thus the most suitable colour for malts must be judged individually for each brewery and type of beer. Pale ale malts usually have a colour between 4 and 6 and mild ale malts between 6 and 8 on the Tintometer scale with the extract wort in a 1-inch cell. The Congress mash with pale lager or Pilsener malts gives 0.17–0.25, with medium pale lager malts 0.30–0.45 and dark lager or Munich malts 0.70–1.00 on the Brand scale. These figures correspond with 2.0–3.0, 3.5–5.0 and 8.0–12.0 with the same malts mashed by the Institute method, using the Tintometer and 1-inch cell.

(175) Cold Water Extract.

This useful determination is prescribed only by the Institute of Brewing. It does not give the percentage of solids extracted from the malt very accurately, since 25 grams of malt of any type is presumed to give a 10% extract with 250 ml. of water, and the solids are estimated by use of the solution divisor, 3.86, (see Section 241) thus,

$$\text{C.W.E.} = \frac{(\text{Sp. gr.} - 1000) \times 10}{3.86}$$

The extraction is carried out at 70° Fahr. using 20 ml. of N/10 ammonia to inhibit enzymic action.

A comparatively high cold water extract is usually associated with good physical modification and a low figure with under-modified malts. Average figures for well-modified English malts are 18.0–20.0%, while percentages between 16.0 and 18.0 generally indicate some degree of under-modification, uneven modification or presence of dead corns. Higher values of 20–22% are often associated with malts made from very mellow barleys, germinated quite normally. Low values may indicate stubborn barleys and, given normal malting conditions, are generally more to be feared than high values when fully modified malt is known to give the best results but in some breweries 17–18% is preferred to 18–19%.

Six-rowed malts of Mediterranean type, malted as is usual in England, do not generally yield more than 15–17% of cold water extract, though held-over and freely growing Californian barleys may give 18%. The lower figure for these malts cannot be entirely ascribed to the smaller percentage of starch in six-

rowed barleys and is paralleled by the smaller percentage of protein converted into soluble products in comparison with two-rowed malts. On the whole, the cold water extract gives a good idea of the degree of modification, with the drawback that stewing conditions on the kiln may give rise to high figures and an appearance of full modification. Care must therefore be taken that the interpretation is not vitiated in this way, while due consideration must be given to the variety of the barley and the range of analytical figures normal to it.

(176) Forced Malt.

Most brewers consider that an unduly high percentage of cold water extract, over 22% in English malts, indicates the defect referred to as "forcing." They ascribe it either to over-modification or to stewing on the kiln and generally associate it with instability in the beer. It no doubt marks a departure from the normal course of malting, which has caused a greater enzymic breakdown than can be met by synthesis of new tissues or by respiration. It may in some cases be associated with abnormality in the barley itself, due to incipient germination accompanying unsoundness. The defects in such malts are generally attributed to undue proteolytic degradation, rather than to excessive carbohydrate breakdown, but it has been shown that high floor temperatures do not favour proteolysis. An increase in the quantity of permanently soluble nitrogen may, however, occur on the kiln and be considerable under favourable conditions (Section 158). This may indicate detrimental changes in the composition of the malt but it is impossible to state what these are or give any explanation of their effects.

On the whole it would appear probable that the defects of forced malt, if and when such really occur, are due to intensive enzymic breakdown and accumulation of intermediate upgrade products. Brown⁴ found that while 40% of the nitrogen of a malt grown under somewhat forcing conditions was found in the extract wort, 46% of that of the germ was extracted under the same conditions. Of the 40% existing as permanently soluble nitrogen, in the wort, 19 and 21 would represent the proportions contributed by the germ and endosperm respectively in this case. The proportion of nitrogen supplied by the embryo and acrospire is thus very high in proportion to its weight, in comparison with that rendered soluble in the endosperm, and may have considerable influence on the brewing quality of a very fully grown malt.

It was formerly held that an excess of assimilable nitrogen, that is nitrogen of low molecular complexity, produced by intensive

modification and, it was believed, by forcing, tended to bacterial instability in beer. This cannot, however, be held to be proved. In some cases it appears to be true, but not in others and the effects of the various factors which determine stability or instability still await investigation. Instability has been shown by Shimweil⁵ to depend on excess of sugars and not of soluble nitrogen in the case of *L. pastorianus*, the organism commonly known as *Saccharobacillus*.

(177) Diastatic Activity.

The Congress methods specify no estimation of enzymic activity, other than determination of "saccharification time." This term, applied to the interval between the attainment of saccharification temperature in the mash and the moment when the wort no longer gives a blue colour with iodine solution, is actually a misnomer, since the conversion to sugars is not complete when iodine normality is reached. The test is made at 10-minute intervals and expressed in 5-minute periods. In the American methods the tests are at shorter intervals, 5, 7, 10 and 5 minutes thereafter, commencing when the temperature has reached 70° C. Pilsen malts generally give iodine normality in 10–15 minutes, Munich in 30–35 minutes.

The English and American methods lay down a determination of diastatic activity by a slightly modified Lintner process,⁶ in which the starch solution is buffered to p_H 4.6. No methods are prescribed for determination of proteolytic or any other enzymic activity. A rather different method of determining diastatic activity, a modification of that proposed by Baker and Hulton,⁷ devised by Windisch and Kolbach⁸ is generally used on the Continent in malt analyses.

The diastatic activity of malt, as measured by the Lintner or Windisch-Kolbach methods, is looked upon by many as of little value in malt analysis. As a measure of converting power this is no doubt true. Mash tun results have little or no relation with the conversion of soluble starch by a cold water extract, as was shown for proteolysis in Fig. 33. The determination also has serious limitations as an indication of the activity of other enzymes, as shown in Table 31, but it does afford some guidance as to the character of the malt. It is correlated with the nitrogen content in any one variety and with the kilning, so that the figure should balance with other determinations in a normally made malt. Thus a high diastatic activity corresponds with a comparatively low extract and a low value combined with a low extract would give rise to suspicion in regard to the germinative activity of the barley. The terms high and low in respect of

diastatic activity must naturally be regarded as relative and dependent on the curing. Hence the diastase should correspond with the colour. Normal figures for English pale malts are between 30° and 40° Lintner, with 25° to 35° for mild ale malts. Pale Continental lager malts generally give around 60° Lintner and pale American malts of Manchuria type 60° – 120° , while dark lager malts give about 30° . Higher values are desirable with increasing percentages of unmalted grain in the grist, not only to ensure adequate conversion but as an indication of the higher nitrogen content required under these conditions.

Some brewers find that a determination of the $[\alpha]_D$ of the extract wort is helpful in the appreciation of malt. It is correlated with the modification of the malt or the ease with which the starch is converted as well as with the enzymic activity and bears a close relation to the $[\alpha]_D$ of the mash tun worts. A low figure corresponds with fuller conversion, or higher maltose percentage on wort solids, than a high result. Examples are given in the analyses in Chapter XII. $[\alpha]_D$ 118° to 122° are normal figures for English malts.

(178) Relation between English and Congress Analyses.

There is no direct relation between analytical results obtained from the same sample by the Institute of Brewing and Congress standard methods of malt analysis, on account of the empirical nature of the methods adopted. Conversion factors would also differ to a certain extent with different malts, because the results in both systems vary with the modification, moisture content, structure of the malt, etc. Thus, for example, the difference in extract due to the coarse and fine grind adopted in the English and Congress methods, respectively, varies with the modification of the malt, its moisture content and with the quantity of husk. The conventional 15 ml. for grains is not equally correct for all malts and involves a discrepancy when compared with mashes made up to a fixed weight of 450 grams. The different mashing temperatures will not influence the extract from all malts equally and the basis of percentage by volume or by weight, with the different meanings attached to extract, both cause discrepancies. Variations due to temperatures at which specific gravities are determined must also be considered. These are 60° Fahr. and 20° C. for the Institute of Brewing and Congress methods respectively. The factors 0.80 or 0.81 serve for approximate conversion of Institute of Brewing to Congress extract with more or less fully modified malts.

The tint given by diluted N/10 iodine or by the Brand synthetic dyes is not the same as that of the 52 series Tintometer

glasses and the relation between them is not quite constant over the range of colour usual in malt analyses. The Tintometer figure varies from about 13 to 15 times the quantity of iodine solution required in ml. per 100 ml. of water to give a match. The Congress wort is also more concentrated than that of the Institute of Brewing methods, so that the comparison of colour is rather complicated. The conversion figure given in Table 52 is the average value obtained in a number of comparative analyses.*

In comparing the results of the Lintner and Windisch-Kolbach methods for determining diastatic activity it should be noted that care is taken in both to limit the production of maltose to 40% of the dry weight of starch used, in order to be within the limits of Kjeldahl's law of proportionality. The Windisch-Kolbach method differs from the Lintner in that a 4% extract of the malt is used instead of 5%, while the conversion is carried out at p_H 4.3 instead of p_H 4.65 and only for 30 minutes in place of 60. The reducing power in the former method is determined by the Willstätter-Schudel iodimetric titration instead of with Fehling's solution and a control for the reducing power of the starch and malt extract is made use of, the last feature being adopted in the American Lintner method. 100 degrees on the Lintner scale represents the diastatic activity of a malt of which 0.1 ml. of the 5% extract will convert sufficient soluble starch under the specified conditions to reduce 5 ml. of Fehling's solution, that is 100 grams of the malt would produce about 820 grams of maltose. 100 grams of the same malt would produce about 400 grams of maltose under the conditions of the Windisch-Kolbach method, which expresses the diastatic power of malt by the number of grams of maltose produced from soluble starch by 100 grams of malt under the specified conditions.

TABLE 52.—CONVERSION FACTORS FOR RESULTS OF INSTITUTE OF BREWING AND CONGRESS ANALYSES

Determination					Institute to Congress	Congress to Institute
Moisture	+ 0.23%	— 0.23%
Extract	× 0.802	× 1.25
Colour	× 0.086	× 11.6
Diastase (Lintner to Windisch-Kolbach)	× 3.50 and then deduct 16	+ 16 and then ÷ 3.50

The diastatic power on the scale used in the Pollak-Egloffstein method is about 20 times that found by the Windisch-Kolbach process. In the former the conversion is carried to three-fifths

of the stage at which the iodine solution becomes brown. If the dextrinolytic activity of the malt is high, this stage will be relatively early in the maltose formation and the rate of the latter will be relatively high. The object of the process is to combine the principles of the Lintner method and the saccharification period, that is to take account of both dextrinolytic and saccharifying components of the diastase.

(179) Summary.

The methods of malt analysis generally used for commercial purposes are entirely empirical. It is consequently necessary that the details of technique should be rigidly standardised in order to ensure comparable results from different analysts. This has been secured by compilations of standard methods by Committees in England, Germany and America respectively. When combined with skilful judgment of the malt, based on its physical characters, these methods have proved adequate for commercial purposes but do not go far enough to establish the brewing quality of the malt without doubt.

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CHAPTER XI

BREWING QUALITY OF MALT AND INTERPRETATION OF MALT ANALYSES

MODIFICATION OF MALT

(180) Malt Quality.

The ultimate criterion of the utility of malt for brewing, to whatever type it may belong, is suitability for producing wort under the existing conditions which shall have the composition, colour and flavour appropriate to the kind of beer brewed and yield a product of adequate stability, both biological and colloidal or physical. That is to say, brewing value cannot be defined by any fixed conjunction of composition and characteristics to cover all cases. There is, however, general agreement in ascribing highest quality to evenly germinated malt of complete friability, good flavour and appearance, made from the best barley as judged by ordinary market conventions and in selecting these for beers of finer quality or greater stability, making use of lower grade barleys for malts intended for quick sale beers. The higher grades thus include malts with low nitrogen content, giving high extracts. The lower quality of the other grades is indicated by inferior appearance, comparable with that of the barley. Such malts generally have a higher nitrogen content, give a lower extract and are usually cured for higher colour. In either case, whatever their appearance or from whatever barley they are made, irregularity of growth and modification means definitely low quality and may lead to trouble in the brewery.

The criteria of "quality" based on appearance and physical examination do not always correspond with the utility of the malt or its brewing value. In some cases it may be necessary to sacrifice quality for utility. For example, it may be desirable to use a malt with greater nitrogen content in order to provide essential yeast nutrients. This almost inevitably means an apparent decrease in quality. Hence "malt quality" as usually understood and "brewing value" are not necessarily the same thing. The assistance of analysis is essential to determine the latter and ability to interpret its findings must be combined with skill in judging the physical characters of malt.

(181) Physical Tests for Modification.

Before analysis became general as a help in determining the quality of malt, great stress was laid on a few simple physical tests by which its degree of modification could be ascertained. It was realised that brewing value depended on satisfactory germination and kilning. This has been emphasised by increasing knowledge of what modification implies and the old tests still retain their usefulness. The length of the acrospire is generally a guide to the extent of modification, but it is not always trustworthy. Its growth becomes more rapid with increasing floor temperatures, and it is possible that full acrospire growth may be attained while part of the embryo is still steely. On the other hand, some corns become quite mealy when its length is comparatively short. Growth can be restricted by withholding air, without hindrance to enzymic conversion in the endosperm, and it lags behind the latter at low floor temperatures. The length of the acrospire is thus not always a true guide to modification, but it provides one of the most useful means of detecting irregularity in the growth of malt, with the accompanying irregularity in modification.

The "sinker" test, which consists in rapidly stirring a counted number of corns into water and ascertaining the percentage that sink, is also extensively used, but it is equally open to serious criticism. The specific gravity of barley is usually between 1.02 and 1.08, while that of malt falls from 1.0 to 0.95 when fully modified, so that barley sinks and lies flat on the bottom of the glass, incompletely modified malt sinks more or less slowly and the corns stand vertically, with their hard ends down, while well-grown malt floats. This is largely influenced by air spaces within the husks, and damage to the latter by polishing may cause many fully grown corns to sink in water and give a wrong impression of their modification. The method can only be taken as a rough sorting test and sinking corns should be examined to make sure of the reason.

Samples should also be bitten down or crushed in a mortar. Their friability is generally a good guide to the extent of enzymic changes, though vitrification may sometimes occur on the kiln. Hard ends can be detected and distinguished from corns which have not germinated or have only partly grown

(182) Modification of Malt and its Brewing Value.

The relation between the modification of malt, as judged by physical tests, and its utility or brewing value may be better appreciated by consideration of the further changes in com-

position which occur in the mash tun. These are essentially a continuation of the enzymic transformations of the carbohydrate, protein and other constituents of barley by which malting is characterised. The processes are carried further in the mash tun until about 75–80% of the dry weight of two-rowed malts becomes soluble, provided the preliminary stages of their preparation have been properly conducted. Under-modification means that the physical condition of the barley and the colloidal state of its constituents have been insufficiently altered. Mashing methods may be varied in such a way as to deal with different degrees of modification but the extent to which it is possible to overcome defects is limited. These two essentials for satisfactory conversion must be considered together and the proper balance between them to secure wort of suitable composition can only be obtained by modification of the malt to an extent appropriate to the mashing method adopted. This is exemplified by differences in the decoction and infusion systems of mashing. The more or less prolonged boil to which part of the mash is subjected in the former renders some of the colloidal constituents of malt much more amenable to the action of enzymes than they would be if merely mixed with water at the moderate temperature of the infusion mash.

For this reason ale brewers would consider most lager malts as under-modified, while lager brewers regard ordinary ale malts as over-modified or even forced. It is a matter of proportion, each type of malt being suitable for the mashing method for which it is intended. There can thus be no definite standard of modification for all malts, and this must be taken into consideration in the physical appraisal of brewing value in which its degree plays such an important part.

The effects of over-modification, that is modification beyond the stage which experience has shown to be most satisfactory for the particular brewing methods or beer for which the malt is intended, are not very clearly understood. They should not be confused with forcing, though the analytical indications may be the same in some respects, such as in an unusually high percentage of cold water extract and permanently soluble nitrogen. There is very little definite information on the effects of too prolonged germination to make any comparison between them and those due to high germination temperatures or stewing on the kiln. This is a good example of the many conditions in brewing which await carefully controlled experimental examination and comparison with analytical determinations. Without such data it is impossible to make the fullest use of malt analysis or to interpret the warnings it may give. It is generally held

that biological instability in the beer is liable to result from over-modification and that the beer will be thin and lacking head-forming properties, both of which are probably due to too great dispersion of colloidal wort constituents or their conversion into crystalloidal substances.

(183) Colloidal State of Malt Constituents.

Further light on the influence of modification on brewing value may be gained by consideration of the nature of the changes in barley constituents which were shown in Chapter IX to accompany the physical alterations. Their effect on the composition of the wort was shown, by reduction in viscosity, to result in change in the colloidal state of its constituents. This general change in physical properties was found to be parallel to chemical changes in some of the chief constituents of the malt. These changes were in the direction of molecular simplification and all apparently came to a stop at about the same time or, it was suggested, were afterwards balanced by processes of synthesis. They were marked by change of insoluble to soluble carbohydrates, of hemicelluloses to soluble pentosans and of proteins to soluble nitrogen compounds. All these changes correspond with increase in the dispersion of substances in a colloidal state and, ultimately, in their conversion to simpler crystalloid compounds.

A number of the essential properties of beer are influenced by the degree of dispersion of its colloidal constituents. The formation of a stable foam is dependent on these and the head-forming capacity is reduced as their dispersion is increased. Production of haze is due to aggregation and precipitation of colloidal particles and stability, in this sense or the length of time over which the beer will remain bright, is increased by molecular simplification of the substances concerned. These properties are attributed in large measure to the proteins and their degradation products, but, to whatever constituent of malt they are due, it appears that increase in the degree of modification results, on the one hand, in reduction in fulness of flavour, and foam formation and retention. On the other hand, it decreases the tendency to precipitation of colloidal particles and increases the physical stability of beer or the length of time it will remain bright, if unattacked by micro-organisms.

These two classes of properties are not equally demanded in all types of beer. Fulness, with head formation and retention, is more important in stouts and many dark beers than permanent brilliance. The latter property is essential in pale beers, particularly if pasteurised, and must be secured, even though it means some loss of fulness and foaming power. It

follows that a more fully modified malt is necessary for stock pale beers and that a lower degree of modification is to be preferred for running ales and stouts. Again, the conclusion is reached that there can be no optimum degree of modification and that judgment must be exercised in selecting malt modified to the correct degree for the particular kind of beer brewed.

It is possible that the most decisive indications of the progress of modification will ultimately be obtained by some measurements related to the colloidal state of the constituents of malt or of its extracts. Reference has been made to Brown's contention that solution of the highly colloidal gum of barley was one of the most significant changes during malting. Uncertainty, however, still exists as to the nature of the substances which cause the high viscosity of worts from under-modified malts and must be enzymically broken down before the malt becomes friable. They may consist largely of hemicelluloses and related substances or, as Piratzky¹ suggests, be of a pectinous nature. This author failed to find any explanation of the highly colloidal state of the worts in their protein, dextrin or pentosan constituents. The substance, of whatever nature it is, that causes the high viscosity of worts from under-modified malts appeared to be removed by precipitation with trichloroacetic acid, since worts with very different viscosities produced from short-grown and long-grown malts had almost the same viscosity, after precipitation and filtration.

Piratzky and Wiecha² found a close relation between the viscosity of Congress extract worts of Continental lager malts and their modification. They obtained values for worts of 10% Plato with a Höppler's³ falling sphere viscometer, ranging from 1.600 cp. for very fully modified samples to 2.187 for short-grown malts, and concluded that the viscosity for normally modified lager malts should be about 1.750 cp. Much more investigation will, however, be required before a decision can be made on the meaning and application of viscosity measurements. The present writer's determinations, with a B.S.I. 1937 standard U-tube viscometer⁴ No. 1, are in agreement to a certain extent with those of Piratzky and Wiecha, giving values between 1.390 cs. and 1.560 cs. for worts of 1030 sp. gr. from English and Californian malts, obtained by the Institute of Brewing method, but they appear to show that factors dependent on the type of malt intervene and complicate the results.

Measurements can be made either in terms of dynamic or kinematic viscosity and expressed as centipoise (cp.) or centistokes (cs.) respectively. Values obtained with the standard U-tube viscometers represent centistokes, which are equivalent to the

quotient of the dynamic viscosity by the density of the liquid, hence $\text{cs.} = \frac{\text{cp.}}{d}$. Determinations are always made at 20° C.,

because the viscosity varies with the temperature, that of water at 20° C. is 1.0068 cs. or 1.0050 cp., the density being 0.99823.

Very useful information in this connection is obtainable from the appearance of the wort obtained for extract determination and the speed at which it filters. A fully modified malt should give a bright filtrate and increasing turbidity will frequently be found associated with decreasing modification. In cases of gross under-modification the filtration becomes very slow.

(184) Analytical Determination of the Degree of Modification.

As analytical methods became more generally used for testing the quality of malts, maltsters naturally began to ask for an analytical criterion of modification in the belief that some determination based on composition would be more satisfactory than the physical tests hitherto relied on. An index or coefficient of modification, based on rigid analytical methods and capable of giving numerical expression to its degree, would clearly be valuable. It is consequently necessary to consider how this requirement can be met, and whether any of the tests yet suggested actually fulfil it or are otherwise useful as criteria of malting quality and utility.

The investigations detailed in Chapter IX on the chemical changes accompanying modification suggest several methods of analysis that might be adopted to measure the progress of enzymic breakdown. They make it clear, however, that no figures obtained by determination of soluble products can completely satisfy the demand for a measure of modification. The opposing processes of breakdown and synthesis were shown to result, in most cases, in attainment of a maximum of soluble products at an earlier stage than that at which the malt is removed to the kiln. Practical experience would seem to indicate that the chemical and physical changes essential in good malt are not completed at that stage. The further changes during kilning must also not be overlooked.

It follows that determinations of soluble products can only be of value, either as an index of modification or criterion of quality in malt, in so far as they correspond with brewing results. The most promising avenue of approach would seem to be through methods based on colloidal chemistry, but these have not yet been brought to such a point that they can be used with

confidence, though interesting results have been obtained by viscosity measurements. Even in the present state of uncertainty the chemical results detailed are helpful to brewers in that they make it possible to obtain a clearer conception of malt composition than was previously attainable. They have shown that the constituents of barley subject to enzymic change all go through a similar sequence of breakdown and synthesis and that the general course of events can be traced by following any one of them. This being the case, analytical convenience must play a large part in deciding which of the soluble products should be measured. It is not feasible in technical analysis to adopt the complicated methods necessary to follow the change in hordein or to estimate the products of hemicellulose breakdown. Much simpler analyses must be adopted and among those that suggest themselves as most likely to be useful are :—

- (1) The difference between the extract of coarse and fine grist.
- (2) The determination of cold water extract.
- (3) Estimation of permanently soluble nitrogen or
- (4) Formol-nitrogen.

The implications of these analyses will therefore be examined individually.

(185) Extract of Coarse and Fine Grist.

A normally modified malt will usually give 1 to 2 lb. more extract when finely ground in comparison with the standard grind. The difference for a less well modified malt may be between 2 and 4 lb. The low extract with coarsely ground malt is due in part, at any rate, to locking up of carbohydrates by protein matter. When the malt is finely ground the granules are liberated from the protein matrix in which they were embedded and more completely converted. The results of this method of analysis are influenced by other factors than modification, such as the diastatic activity and kilning, but they agree fairly well with other criteria of modification and are very useful in the appraisalment of malt. Figures⁵ showing this for some Californian Atlas malts experimentally malted in a similar manner are given in Table 53.

A Seck mill at the standard setting of 0.5 mm. was used for the coarsely ground Californian malts in Table 53 and a coffee mill for the fine grind. The latter is rather unsatisfactory for the purpose as the grind cannot be standardised. The examples of coarse and fine grind extracts in Table 57 are of malts ground by the Seck laboratory and fine meal mills set with the Congress

sieves. Those in Table 54 represent malts ground with the Wiley mill with 2 mm. and 0.5 mm. sieves. This mill consists of a set of knives which revolve very closely to another set and cut the grain. Immediately the particles of the latter are small enough they pass through an accurately gauged sieve into the receiver tray, while the remainder continues to be cut until it also is reduced to the same degree of fineness.

TABLE 53.—EXTRACT OF COARSE AND FINE GRISTS, CALIFORNIAN ATLAS MALTS

	A	B	C	D	E
Extract on dry malt lb. coarse	96.0	95.4	93.7	91.5	88.3
Extract on dry malt lb. fine	96.6	97.5	95.8	94.0	92.0
Ratio of coarse and fine extract	99.4	97.8	97.8	97.3	96.0
Nitrogen % of dry barley	1.300	1.398	1.555	1.612	1.958
P.S.N. % on dry malt ..	0.359	0.332	0.356	0.350	0.423
P.S.N. as % of Barley N ..	27.6	23.7	22.9	21.7	21.6
Cold water extract % ..	17.3	16.1	15.0	14.5	15.7
Diastatic activity Lintner °	29.0	28.0	28.5	31.0	35.0

TABLE 54.—EXTRACT OF COARSE AND FINE GRIST (WILEY MILL) COMPARED WITH P.S.N. AND C.W.E.

	English Pale	English Mild	English Lager	Californian	
				1	2
Extract Wiley, 2 mm. dry	102.9	97.2	102.2	95.5	94.7
Extract Wiley, 0.5 mm. ..	103.3	100.5	103.4	96.1	95.7
Increase %	0.39	3.39	1.17	0.63	1.06
Extract Seck 0.5 mm. ..	102.3	98.8	103.0	94.8	94.5
P.S.N. % of total N ..	39.3	34.9	36.0	28.6	26.2
Cold water extract % ..	18.5	17.8	17.8	15.2	13.6

(186) Cold Water Extract.

The figures given in Chapter IX for the changes in cold water extract during germination suggest that it should prove a useful indication of the progress of modification. This is generally found to be the case, as is shown in Tables 41, 53, 54, and in several analyses given in later sections. The influence of kilning conditions is, however, rather marked, making it sometimes difficult to decide whether the increase in cold water extract is due to normal growth and modification or to stewing on the kiln. Nevertheless the information gained by this determination

in conjunction with other data is very helpful in the valuation of malt.

Hartong⁶ has devised a method for obtaining an estimate of the degree of modification of malt by mashing at various temperatures and comparing the extracts obtained with the Congress extract, whereby he obtains some measure of the action of the enzymes operating at these temperatures on various malt constituents. 50 grams of the malt is finely ground and continuously stirred for 1 hour at 25°, 45°, 65° and 85° C. The mashes are then rapidly cooled on ice and made up to 450 grams. The first three are filtered but the mash made at 85° (185° Fahr.), contains a lot of liquefied but unconverted starch and cannot be filtered. It is poured into a tall cylinder and allowed to stand over-night, after which the liquid is poured off and filtered through cotton wool. The specific gravities and extract are then determined by means of the Plato Table and compared one with another and with the Congress extract. Results obtained with a malt taken off the floor at 7, 8 and 10 days were as follows:

TABLE 55.—EXTRACT OBTAINED FROM MALT AT VARIOUS TEMPERATURES
SAMPLES TAKEN FROM FLOOR ON THE 7TH, 8TH, AND 10TH DAY

EXTRACT PER CENT.					
C.	25°	45°	65°	85°	Congress
7 days ..	22.4	28.0	79.2	71.6	80.5
8 days ..	23.7	29.9	78.7	71.0	79.5
10 days ..	27.1	34.9	78.3	69.6	79.8
PER CENT. OF CONGRESS EXTRACT					MEAN VALUE
7 days ..	27.8	34.8	98.4	88.9	62.5
8 days ..	29.8	37.6	99.0	89.3	63.9
10 days ..	34.0	43.7	98.1	87.2	65.8

The results are used in the following manner. The extracts found at the four different temperatures are expressed as a percentage of the Congress extract, which is regarded as the maximum. The mean value of the four percentages is then calculated. Hartong finds that this lies between 60 and 70 for Continental lager malts and he refers to the excess over 58 as the modification figure (*Losungszahl*).

At 25° C. (77° F.) there is slight action by such enzymes as phytase and protease. At 45° C. (113° F.) the protease is active and at 65° C. (149° F.) all the enzymes work strongly. At 85° C. (185° F.) all the enzymes, with the exception of the

liquefying factor of diastase, are destroyed. The latter still retains some activity and the wort obtained at 85° C. contains liquefied unconverted starch.

(187) Products of Protein Breakdown.

The degradation products of the proteins of barley appear to have more far-reaching effects on the properties of wort and beer than those of any other enzymic change. For this reason they have been more fully studied than others and are attractive as a possible source of information on the degree of modification. The relation between the brewing quality of malt and the quantity of nitrogen extracted from it during mashing has been realised for a long time. Thus it was stated by Schjerning⁷ as early as 1910 that a general malt analysis does not yield sufficient data for a real valuation of its quality. For this, he contended, it was necessary to know whether the protein conversion was regular and completed. Schjerning was very emphatic in giving analytical criteria. He considered that a perfectly normal and complete conversion had been attained when a malt gave in the Congress analysis wort,

(1) At least 33% of its total nitrogen in the form of soluble nitrogen ;

(2) At least 27% of its total nitrogen in the form of proteolytic decomposition products, and

(3) When the laboratory wort did not contain any protein matter belonging to the group which he called Albumin 2.

Schjerning's contentions have been borne out in essentials, though his methods of fractionation of wort nitrogen are no longer held to be very satisfactory. They have been amplified in details by more recent investigations and embodied in practice in the "coefficient of modification" based on permanently soluble nitrogen. It is not yet possible to be very definite in ascribing good or bad qualities to this or that constituent among the protein breakdown products, but it is generally held that there is a decrease in what may be called the colloidal properties of wort and beer as modification proceeds. This is accompanied by a reduction in the quantity of substances in such a colloidal state that they prevent a satisfactory break in wort or give turbidity in beer. Among these are colloidal nitrogenous substances which can be only partly removed from the wort during boiling and cooling and exist in beer in such an unstable state of equilibrium that only time or small changes in temperature or reaction are required to bring about coagulation and precipitation.

The choice of simple analytical methods for determining the

quantity of protein breakdown products is at present limited to estimation of soluble, permanently soluble, coagulable and formol nitrogen, among which the permanently soluble nitrogen has been found most useful. A determination of formol-nitrogen might appear more definite as an indication of the degree of protein breakdown, but the analysis is rather delicate and the results are generally approximately parallel with permanently soluble nitrogen and, for the present purpose, appear to offer no advantages. The formol-nitrogen in extract worts from English malts is usually about 20–25% of the P.S.N., the percentage increasing with fuller modification, but it is rather lower with six-rowed Mediterranean type malts.

It has been pointed out that the ready-formed soluble or permanently soluble nitrogen in malts can only be determined by analysis of extracts with very cold water. It is much more convenient to make use of the extract wort and numerous analyses have shown that very similar conclusions are reached by use of the hot mash in place of cold water extracts. The course of events revealed by the two analyses is very similar, although the proportions of the various nitrogen fractions are different. Owing to proteolysis at the higher temperature, the permanently soluble nitrogen of the hot mash is usually about one-third higher than that extracted by ice-cold water. The figures in Table 56 provide a comparison of results obtained by extraction at different temperatures of two malts from similar Spratt-Archer barleys.⁸ A was fully modified and contained 1.45% of nitrogen on dry matter. B was definitely under-modified and had a nitrogen content of 1.51%.

TABLE 56.—NITROGEN EXTRACTED FROM WELL-MODIFIED (A) AND UNDER-MODIFIED (B) MALTS AT VARIOUS TEMPERATURES, AS PER CENT. OF TOTAL NITROGEN OF MALT

Temp. of mash	Permanently soluble nitrogen		Coagulable nitrogen		Total soluble nitrogen	
	A	B	A	B	A	B
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
32° F. ..	25.5	18.7	6.4	10.2	31.9	28.9
70° F. ..	28.1	24.5	5.0	6.1	33.1	30.6
140° F. ..	40.4	36.0	1.4	2.0	41.8	38.0
150° F. ..	39.7	33.3	0.7	0.7	40.4	34.0
160° F. ..	34.8	30.6	0.0	0.0	34.8	30.6

The most convenient method for expressing nitrogen fractions is as a percentage of the total nitrogen of the malt. The

calculation with the Institute of Brewing wort is based on the assumption that the latter is a 10% extract of the malt. Thus 0.05 gram of P.S.N. in 100 ml. of the wort is equivalent to 0.5% on the malt and would be 33.3% of the total nitrogen with a malt containing 1.5% of nitrogen. The calculation from the Congress wort is rather different, as the mash is made up to 450 grams. The weight of the wort is consequently 450 grams less the weight of the grains. The latter is 50 grams less half the moisture content of the malt, less half the extract per cent. calculated from the Plato Tables. If a measured volume of wort is taken for nitrogen determination, its weight must be calculated from the specific gravity before the nitrogen found is calculated back to the malt.

It is necessary to adopt a standard method of boiling the wort in order to obtain consistent results. Thus 200 ml. of the wort may be boiled for 15 minutes, excessive diminution of volume being prevented by adding sufficient water before boiling to ensure that the final volume shall be about 150 ml. The boiled wort is returned to the 200 ml. flask, cooled to 60° Fahr., made up to volume and filtered. The nitrogen is determined in 25 or 50 ml. by the Kjeldahl-Gunning process.

This method of boiling does not completely precipitate coagulable nitrogen. More complete precipitation is secured by boiling the wort under a reflux condenser for 5 hours in a bath of saturated salt solution, as suggested by Windisch, Kolbach and Vogl,⁹ but the simpler process is generally adopted.

It will be noted from the figures in Table 56 that the coagulable nitrogen in the hot mash is much reduced in comparison with that in the cold extract. This depends largely on coagulation during mashing but also, in part, on further degradation of coagulable proteins. Since this reduction is liable to vary, and with it the quantity of soluble nitrogen, determination of permanently soluble nitrogen is to be preferred to that of the remaining soluble nitrogen, though the latter is frequently used. The figures in Table 57 from analyses of Congress worts by Kolbach¹⁰ are typical of results obtained. They show that the percentage of nitrogen that becomes soluble in the hot wort remains practically constant during the latter half of the flooring period, just as was found to be the case with the ready-formed soluble nitrogen of malt. They also show that the total nitrogen of the malt may increase slightly in some cases and decrease in others as germination proceeds. As a result, the soluble nitrogen when expressed as a percentage of the total nitrogen remained constant during the last three days with malt A, but increased during the last two days with B.

TABLE 57.—SOLUBLE NITROGEN OF MALTS AT DIFFERENT STAGES OF GERMINATION

CONGRESS MASH

Days' germination	Malt A			Malt B		
	7	9	10	6	8	9
Nitrogen % on dry malt..	1.770	1.806	1.821	1.726	1.696	1.681
Soluble N % on dry malt	0.596	0.607	0.613	0.659	0.696	0.700
Soluble N as % of total N	33.7	33.7	33.7	38.2	41.0	41.6
Extract % Fine ground ..	79.5	79.2	79.3	81.2	81.0	81.1
„ Coarse ground	78.1	78.0	78.1	80.4	80.7	80.8
„ Difference ..	1.4	1.2	1.2	0.8	0.8	0.3
Appearance of wort ..	sl. opal	clear	clear	sl. opal	clear	clear
Average acrospire length						
%	63	69	77	—	—	—
Sinkers %	46	38	24	—	—	—

Extract lb. per quarter = % Extract \times 0.8

The increasing physical modification of A, while the soluble nitrogen remains practically constant as a result of the balance of down-grade and up-grade processes, is shown by the fall in the percentage of sinkers, by increase in the length of the acrospire and, less clearly, by decreasing difference between the extracts of the finely and coarsely ground malt. The figure for acrospire length is the sum of the products of the percentages of corns in which the growth was $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, $\frac{5}{8}$, 1 and $5/4$ ths of the corn length by the respective lengths of the acrospires. Thus

$$2 \times \frac{1}{4} + 33 \times \frac{1}{2} + 51 \times \frac{3}{4} + 10 \times \frac{5}{8} + 4 \times 1 + 0 \times \frac{5}{4} = 62.5$$

It is essential that the method of mashing adopted in determinations of soluble or permanently soluble nitrogen should be specified, on account of the different results obtained. It is advisable to adhere to one or other of the standard methods, for which comparative results are given in Table 58. The permanently soluble nitrogen of the malt calculated from the Congress wort is usually about $\frac{1}{5}$ or $\frac{1}{4}$ greater than if the determination is made in wort from the Institute of Brewing extract mash, on account of the lower initial mashing temperature of the former and greater proteolysis.

The figures in the columns headed P.S.N. % of total N corresponded with the modification of the malts, so far as that could be judged by physical examination, a higher figure representing fuller modification. Analyses of a large number of commercially-made malts show that 36–38% of permanently soluble nitrogen on total nitrogen is a normal figure for

well-modified malts made from English barleys, and that malts giving lower figures are less fully modified or contain a proportion of dead or slightly grown corns. The following points should also be noted.

The "normal" figure for P.S.N. as % of total nitrogen varies in different varieties of barley and is considerably lower in six-rowed barleys of Mediterranean type than in two-rowed barleys. 30% in Californian malts corresponds with 36% in English malts.

Barleys with a higher nitrogen content give lower figures than low nitrogen barleys of the same variety when malted in a comparable manner. This corresponds with the increasing stubbornness usually associated in the maltings with greater nitrogen content.

TABLE 58.—PERMANENTLY SOLUBLE NITROGEN OF MALTS
(% ON DRY MALT AND % ON TOTAL NITROGEN)

INSTITUTE OF BREWING AND CONGRESS ANALYSES

Malt	Total nitrogen % of malt	Inst. of Brewing		Congress	
		P.S.N. % of malt	P.S.N. % of total N	P.S.N. % of malt	P.S.N. % of total N
1 English	1.280	0.505	39.4	0.654	51.1
2 „	1.475	0.534	36.2	0.650	44.0
3 „	1.472	0.521	35.4	0.600	41.1
4 „	1.595	0.529	33.2	0.616	38.6
5 „	1.625	0.476	29.3	0.606	37.3
6 Californian	1.305	0.404	31.0	0.496	38.0
7 „	1.585	0.463	28.8	0.560	36.0
8 „	1.561	0.403	25.8	0.534	34.2
9 French lager	1.455	0.415	28.5	0.510	35.0
10 Danish lager	1.846	0.506	27.4	0.594	32.2
11 Canada Western (Diastatic Malt)	2.206	0.650	29.5	0.809	36.7

(188) Coefficient of Modification.

It has been shown in this survey of available methods for obtaining a numerical expression of the degree of modification that no method based on determination of soluble products of enzymic breakdown is quite satisfactory, since modification apparently proceeds after the maximum quantity is found. It is believed that physical methods based on measurement of the colloidal state of malt or wort constituents will probably ultimately be found the most useful, but these have not yet been so fully studied as the chemical processes. The determination of the difference between the extracts of coarsely and finely

ground grist does afford some information on the colloidal state of malt constituents and has proved a very good index of modification, approaching more closely to a measure of physical modification than the chemical methods. It, however, demands standard mills of a precision beyond that found in many laboratories in order that the results may be consistent and reproducible.

Of the chemical methods, the determinations of cold water extract and permanently soluble nitrogen are the simplest and most readily standardised. The cold water extract appears to be more subject, under normal malting conditions, than the permanently soluble nitrogen, to influences on the kiln, which introduce considerations somewhat apart from the usual interpretation of modification. The P.S.N. also has the advantage of very close correlation with wort and beer properties that are intimately associated with protein breakdown and modification in the chemical sense. At present it holds the field as the most generally useful determination, and has been specifically referred to as the Index of Modification.⁸

Considerable experience of its application in malt analysis has led to the conclusion that the figure obtained by expressing the permanently soluble nitrogen of the hot mash wort as a percentage of the total nitrogen of the malt is remarkably closely correlated with the modification of the malt, as judged by physical and other tests, and can be used with considerable confidence as an indication of the utility of the malt and of the behaviour of the beer made from it. It is not a measure of the full extent of the changes undergone by the proteins during malting, but only an expression of the balance between down-grade and up-grade processes, which may be reached before modification is complete. Yet it serves for practical purposes as a very useful index or coefficient of modification.

The term "index of modification," as applied in this way, may be criticised and has been qualified as "index of protein modification" or the "permanently soluble nitrogen index of modification," but the former is not any more accurate as a description of what is measured by the permanently soluble nitrogen than the original term and the latter is cumbersome, though more precise. "Coefficient of modification" is perhaps more satisfactory, suggesting something that acts with or is correlated with modification but, to avoid uncertainty, the analytical results should be expressed simply as P.S.N. % of total nitrogen.

The following points may be noted in connection with the use of this empirically derived "coefficient of modification" as an indication of the quality of malt or its behaviour in brewing.

(1) English malts of proved good brewing quality for pale or mild ales, containing about 1.4–1.6% of nitrogen, made from good quality, fully mature barley, normally and evenly modified as judged in other ways, usually give 36–38% of P.S.N. on total nitrogen.

(2) Such malts have proved suitable for brewing beers of lasting brilliance in bottle. Percentages of 38–40 are in some cases preferred, while 34–36% indicates greater properties of fulness and head retention but less protein stability.

(3) A lower percentage is usually associated with incomplete modification, with uneven growth due to a proportion of immature or prematurely ripened barley in the bulk or to the presence of thin or unmalted corns.

(4) Malts with these defects are definitely of lower brewing quality and as the P.S.N. percentage approaches 30 they become increasingly liable to give beer with defects due to the presence of colloidal constituents in a low state of dispersion, such as difficulties in fermentation and fining or an early haze formation.

(5) A high percentage, readily obtained by normal malting methods, distinguishes mellow barley from immature or prematurely ripened grain. It may sometimes be associated with unsoundness in the barley.

(6) The percentage usually corresponds with the friability of the malt.

(7) A low percentage is often associated with lack of brilliance in the analysis wort, and sometimes with a wort that will not filter bright even after boiling. It is difficult to get a percentage as high as 34–36 with English barleys containing over 1.65% of nitrogen.

(8) With Californian and similar six-rowed malts, a percentage of 30–32 corresponds with 36–38 given by two-rowed malts.

INTERPRETATION OF MALT ANALYSES

(189) Nitrogen Content of Malt.

The significance attached to the nitrogen content of barley and malt suggests that the standard methods of analysis are incomplete in an important respect and inadequate to give all the information obtainable by simple methods. The other determinations are related so closely to nitrogen content that, given reasonable skill in the physical examination of malt, with ability to judge its colour, moisture content and modification from the bite, it is possible to calculate the extract with very close approximation from the nitrogen content and size of the

corns and write the ordinary standard analysis with fair confidence from this one determination only. The same applies to the extract. Given that one determination, it is possible to calculate the nitrogen content and base the other figures on these and on the friability and flavour of the malt. This intimate relation between the various analytical determinations in a normal malt is the basis of their interpretation, while abnormalities, usually meaning some defect in the malt, can be detected if nitrogen determination is added to the standard analyses.

The influence of nitrogen content on quality applies equally to malt as to barley. Insistence on its importance does not mean that the effects on quality of constituents other than nitrogenous substances are overlooked but, rather, that they are less well known. Some of the properties of malt and wort generally attributed to nitrogen in some of its forms may quite well ultimately be found to depend on other substances. The nitrogen content can, however, be determined accurately and consequently becomes the centre point of the interpretation of analyses as well as a key to the quality of malts.

It is impossible to state an optimum nitrogen content to cover malts for all purposes. Malts of similar type, graded according to appearance and other physical properties, usually show a corresponding gradation in nitrogen content and fall into groups suitable for different purposes. Thus fine malts with 1.2 to 1.4% of nitrogen are suitable for higher gravity, all-malt ales, while 1.5 to 1.7% of nitrogen is to be preferred as the percentage of unmalted grain increase to about 25% and malts with 1.8 to 2.0% are desirable with greater proportions of malt adjuncts, if they can be obtained sufficiently well modified. The gravity of the wort must also be taken into account when deciding on the most appropriate nitrogen content, because a certain minimum quantity of nitrogenous yeast nutrients is requisite and lower wort gravity means dilution of those present. A difficulty in selecting English malts for lighter beers arises from the frequency with which the required quantity of nitrogen is accompanied by defects due to uneven or inadequate modification. All the desirable properties dependent on nitrogen content, including flavour, head retention and yeast nutrition, can be secured in stronger beers from low nitrogen malts, which should have none of the defects so common in higher nitrogen malts and give high extracts.

It is necessary to take the variety of barley and the place where it was grown into consideration when judging the implication of its total nitrogen content. American barleys of Manchuria type malt easily with 2.0% of nitrogen and make good malts of

their kind. Malt with an equally high nitrogen content from other barleys would almost certainly be rejected for ale brewing, even if it had not been condemned as barley. In almost all cases an English or Californian malt with over 1.7% of nitrogen will be found to have presented difficulties in malting and to be under-modified. About 1.6% of nitrogen is considered excellent in Continental pale lager malts. 1.8 to 2.0% is required to give the full flavour of Munich malt.

(190) Use of Permanently Soluble Nitrogen Determination.

Although a permanently soluble nitrogen percentage of 36 on total nitrogen was mentioned as a kind of datum line for estimating the degree of modification in English malts, there is no suggestion that it marks a rigid demarcation between good and poor brewing quality. It is about the average figure for two-rowed English malts of ordinary good quality and modification. Higher figures appear to be correlated with more extensive change in the colloidal state of the various malt constituents extracted in mashing and lower figures apparently mean that some exist in a comparatively low state of dispersion in the wort. The properties of beer materially depend on this feature of wort composition. High dispersion tends towards lasting brilliance but may, if pushed too far, cause a lack of fulness and head retention. Insufficient change in colloidal character involves a tendency to precipitation of particles existing in a low state of dispersion, producing excessive sediments, protein haze in beer and, possibly, yeast coatings. Intermediate conditions appear to be favourable to fulness of flavour and foam stability.

Hence there can be no standard coefficient of modification, appropriate to all kinds of beer. Malts with higher or lower values would be selected according as lasting brilliance or characters depending on colloidal properties are desired. A high value may be essential for carbonated, bottled pale beers, but a lower figure would be preferred for stouts and most draught ales. Requirements with different brewing processes also vary. Some, the decoction mash in particular, deal adequately with less fully modified malts than others.

Other qualifications have to be considered in connection with the variety of the barley. It has been shown that the permanently soluble nitrogen of Californian and other six-rowed malts of similar type is considerably lower than that of English malts of the same nitrogen content when comparably malted. A datum line of 30 for Californian malts corresponds with 36 for English. Further, high nitrogen barleys do not normally yield such a high proportion of their total nitrogen in the soluble

form as low nitrogen barleys of the same variety. It is difficult to get a coefficient of modification of 36 with English barleys containing 1.6% or more of nitrogen on dry matter. This may be taken as an indication of the lower malting quality of such barleys, and must be borne in mind when comparing the figures given by different malts.

A significant feature of this coefficient of modification is its value as an indication of the purpose for which the malt is most suitable, when considered in relation with other analytical data or criteria of quality. Having decided on the most satisfactory percentage of permanently soluble nitrogen on total nitrogen for any particular beer and brewing method, it is possible to select barleys which should yield these figures when malted. Failure to obtain the desired percentage on total nitrogen may be due to immature or unscreened barley or unsuitable malting procedure. The analyses given in Chapter IX show that attempts to raise the percentage by higher floor temperatures or forcing methods are likely to fail and that a slow and steady germination during the first half of the flooring period would probably be more effective. The germinative activity of the barley must be taken into account. Thus a vigorously growing barley, with high proteolytic activity, may be germinated at considerably higher temperatures than would be permissible for one in which the growth is less active and enzymic development lower.

It has been pointed out that the quantity of permanently soluble nitrogen extracted from a malt varies with the conditions of mashing, and that considerably more is extracted in a decoction than in an infusion mash. Hence a malt that might appear under-modified for infusion mashing, in the sense that it yields too little of its total nitrogen in soluble forms, might be quite adequately modified for a decoction mash.

The figures in Table 59 will serve as a guide to the interpretation of analyses. They must be read with due regard to the purpose for which the malt is intended. Hence the descriptive terms are only relative to their application, but the figures to

TABLE 59.—P.S.N. % OF TOTAL N AS A "COEFFICIENT OF MODIFICATION"

		2-rowed malts	6-rowed malts
1. Very fully or over-modified	..	41	34
2. Well modified malts	40-36	33-30
3. Moderately modified	35-32	29-26
4. Low or under-modified	31-	25-

which they are applied will generally be found to correspond with the friability of the malt. Only one set of figures is given to cover all malts, whether for ale or lager. If they are applied to lager malts, it must be noted that they refer to analyses made by the Congress method, and that they refer to soluble nitrogen and not permanently soluble, ale malts being analysed by the Institute of Brewing method to obtain the figures given.

Kolbach found that the soluble nitrogen of the Congress wort from a large number of lager malts varied between 32 and 48% of the total nitrogen of the malt, averaging 38%. He considered that over 41% represented very good modification, between 35 and 41% good modification, and below 35% only moderately modified. The coagulable nitrogen of the Congress mash averages about 5% of the total nitrogen, so that these figures should be reduced by about 5 to give permanently soluble nitrogen. Since the solubility of coagulable nitrogen may be influenced by the increasing quantity of soluble salts in the malt as modification proceeds, Kolbach and Antelmann¹¹ later stated that a comparison of protein modification could only be made by means of the permanently soluble nitrogen.

(191) Yeast Nutrition.

The absolute quantity of permanently soluble nitrogen in the analysis wort should also be considered in connection with yeast-nutrient requirements. It is helpful to express it for this purpose as a percentage on wort solids, since allowance can then be made more easily for the gravity of the wort. This point is returned to in Section 206, in connection with the selection of malt for different kinds of beer, but it should be noted that a higher percentage on wort solids is required in light gravity beers than in stronger, in order that the minimum requirements should be met in the former. It is not possible to give definite minimum figures, which must vary according to other conditions, but suggestions are made in the Section referred to. It is also possible in some cases that the quantity of permanently soluble nitrogen found is fallacious as an expression of yeast-nutrient qualities, since the latter do not depend on it in its entirety but rather on the proportion in the simplest molecular forms. The quantity of formol-nitrogen present is probably a good guide to these and, since the percentage of formol-nitrogen in the permanently soluble nitrogen tends to fall with decreasing modification, a higher permanently soluble nitrogen in a badly modified malt may actually contain less directly assimilable nitrogen than a lower permanently soluble nitrogen in a more fully modified malt.

(192) Application of Extract Prediction Equations.

Interpretation of the results of extract determinations rests on their correlation with the malt type, nitrogen content and size. It usually involves consideration of whether the highest extract consistent with its type has been secured and, sometimes, whether variations through a large bulk or contract are due to unavoidable differences in the included growths of barley or to some defect in malting or mashing. A modification of Bishop's extract equation

$$E = A - 10.5 N + 0.2 G$$

can be usefully applied to analyses by the Institute of Brewing standard method. It is only rarely that a direct comparison can be made between barley and malt and it is necessary slightly to alter the constants in the equation when it is applied to malt analyses to allow for an average loss of nitrogen content and thousand-corn weight during malting. The following modified equation has been found suitable for the purpose.⁸

$$E = A - 10.6 N + 0.22 G$$

This equation can be used in two ways: (1) If the varietal factor of the barley malted is known, this can be substituted in the equation with the nitrogen content and thousand-corn weight of the malt, both on dry basis, and the extract calculated. This is compared with the extract found, also on dry weight. (2) It is frequently more convenient to substitute the extract found on dry malt, the nitrogen content and thousand-corn weight in the equation and calculate A. This gives a more striking comparison between different malts and valuable information on the malt under examination when this "extract index" is compared with the known average value of A for its type.

Normally modified malts of the same type have been found to give remarkably consistent extract indices in any one season and over a number of seasons, so that it is possible to base conclusions on variations from the average value obtained with particular samples. In normal seasons 108.5 and 108 have proved to be suitable comparison values of A for English and six-rowed Californian malts respectively. 108.5 has been found more accurately to represent the extract index of Spratt-Archer than Plumage-Archer malts, for which 108 is more usual. 101 and 102 are better values for some six-rowed Mediterranean type malts than 108, while 106-107 is closer to that usually obtained with American Manchuria malts. In some cases a small alteration in these figures to correspond with the average of the malts made or used may be found necessary. Values of 109-110 have

been found more characteristic for English malts in seasons, such as 1936, when the barleys modified more easily than usual. The standard of comparison is soon found each season, and low values can generally be traced to some defect in the malt or barley or to under-modification.

Analyses by the Congress methods can be examined in the same way, using the equation given in Section 74,

$$E = A - 0.85 P + 0.15 G$$

and the varietal constants 84 and 79 for two-rowed European and six-rowed Californian malts respectively, or the modification of this equation found by trial to be most appropriate. *P* represents protein in this equation and all values used or calculated are on moisture-free basis.

(193) Summary.

Quality in malt is generally judged by its regularity of germination, friability and appearance. High quality usually means a malt made from the finest barley of its type, with a low nitrogen content. These criteria do not necessarily coincide with the brewing value of the malt. For many purposes a malt with a higher nitrogen content and inferior appearance is to be preferred. Among the most important factors in brewing value is the degree of modification of the malt, but requirements differ according to the brewing methods and type of beer. It is consequently desirable to have analytical methods by which the modification can be measured. Physical or chemical methods might be applied for this purpose, since the effects of variations are due to differences in the colloidal state of substances extracted as well as to their chemical composition. Very promising results have been obtained by measurement of the viscosity of the extract wort and useful information is given by the difference between the extracts of coarsely and finely ground malt.

There are restrictions on the applicability of chemical methods. but determination of the protein degradation products in wort and of the cold water extract have been found to give results which are very concordant with the physical appraisal of modification. The permanently soluble nitrogen expressed as a percentage of the total nitrogen of the wort is used as a "co-efficient of modification," being preferred to determination of other enzymic breakdown products, on account of its usefulness in other directions. Its utility for assessing modification depends on its correlation with properties of the wort and beer made from the malt in question. There is now a good deal of evidence

from breweries that this coefficient of modification does in fact serve to indicate the brewing value of the malt, and the purposes for which it is suitable.

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CHAPTER XII

TYPICAL MALT ANALYSES AND THEIR INTERPRETATION

ALE MALTS

(194) Analytical Criteria of the Quality or Brewing Value of Malts.

The analyses collected in the following pages have been selected either as representative of various types and grades of malt or to illustrate how certain defects can be detected from analytical results. They were carried out strictly in accordance with the standard methods of the Institute of Brewing or Congress, as the case may be, with additional determinations of total nitrogen, permanently soluble nitrogen and thousand-corn weight. Their interpretation is based on

- (1) Considerations arising from the standard determinations.
- (2) Correlation of these results by means of the total nitrogen content.

(3) Comparison of the extract obtained with the potential extract, calculated from the modified prediction equation.

(4) Consideration of the relation between the permanently soluble nitrogen and the total nitrogen content of the malt.

(5) Inferences on the degree of modification based on the total nitrogen, permanently soluble nitrogen, cold water extract and extract. In some cases comparisons are made between the extracts of coarsely and finely ground grists.

(6) In all cases it is assumed that a critical physical examination of the malts was made.

(195) English Pale Ale Malts.

The first two analyses in Table 60 are representative of fine English pale ale malts. They are well balanced, as shown by correlation of the results of the standard determinations with the nitrogen content and thousand-corn weight. The extracts on dry malt correspond with those calculated from the equation

$$E = A - 10.6 N + 0.22 G$$

using the varietal factors 108·5 and 108·0 for Spratt-Archer and Plumage-Archer respectively. The nitrogen content is low in both cases, corresponding with high-class barleys of fine appearance. The permanently soluble nitrogens are rather low for light gravity beers and suggest that lack of yeast nutrients would result if more than a very small proportion of unmalted cereals or sugar was used with them. These malts are particularly suitable for all malt beers of good gravity, the permanently soluble nitrogen being typical of normally malted, well-modified English malts, as shown by its percentage of the total nitrogen. The cold water extracts and extracts, the latter agreeing with those calculated, also correspond with full but not excessive modification. The diastatic activities and $[\alpha]_D$ are also normal and agree with the curing as indicated by the colours, which are suitable for pale ales of fairly high gravity.

TABLE 60.—ENGLISH PALE MALTS

	Spratt- rcher (1)	Plumage- Archer (2)	Same bulk of rather small, fine Spratt- Archer barley	
			(3)	(4)
Moisture %	1·5	1·8	2·0	2·0
Extract, lb. 336 lb.	100·5	100·6	98·4	98·5
Colour, 1-inch cell	4·5	4·0	5·5	6·0
Cold water extract %	18·0	18·7	18·5	19·0
Diastatic activity, L°	36·0	37·0	35·0	38·0
$[\alpha]_D$ of wort solids	118·5	119·0	121·5	119·0
Extract, on dry malt	102·0	102·4	100·4	100·5
Total N % „ „	1·342	1·314	1·458	1·471
P.S.N. % „ „	0·510	0·509	0·494	0·577
„ % on total N	38·0	38·7	34·6	39·2
„ % on wort solids	0·67	0·67	0·66	0·77
1000-corn dry weight, gr.	35·3	38·0	31·6	31·8
Calculated extract	102·1	102·4	100·0	99·9
Extract index	108·6	108·0	108·9	109·1

Nos. 3 and 4 were made from the same barley, and are good examples of differences in analytical figures due to varying degrees of modification. It would be judged from the cold water extracts and $[\alpha]_D$ that No. 4 was more fully modified than No. 3. This is borne out by its greater permanently soluble nitrogen and also by the extract. The extract comparison is made by substituting the extracts, nitrogen percentages and thousand-corn weights in the above equation and calculating A

as the extract index. This shows a difference of 0.2 lb. in favour of No. 4, although its nitrogen content is slightly greater than that of No. 3. The difference between the two extracts is, however, so slight as to be within the limits of experimental error, but taken in conjunction with the other figures, appears to be significant. The extract indices are higher than is usual for Spratt-Archer in normal years, 108.5, but are typical of the barleys of 1936 which malted very easily, as is also shown by the cold water extracts.

The inferences to be drawn from the permanently soluble percentages of the total nitrogen, namely 34.6 and 39.2, are that No. 4 was more fully modified than No. 3, but not that it was necessarily a better malt on that account. The choice would depend on the use to which the malts were to be put. The figures for No. 3 indicate that it is a satisfactory malt for some beers and would probably be chosen for naturally conditioned pale ales, particularly for draught purposes. No. 4 would, on the other hand, be selected for carbonated bottled beers if brilliance over a long period of storage was required. 39.2 is not so high as to suggest instability due to over-modification. The good agreement between the cold water extract, extract, permanently soluble nitrogen and its percentage of the total nitrogen in relation with modification in each malt will be noticed. No figures for the extract of finely ground grist or for the wort viscosities are available, but they would probably correspond with the other determinations.

Low molecular protein degradation products are among the most important yeast-nutrient substances in wort and at the present time there is no better analytical method of comparing their relative quantities in different worts, often referred to as the yeast-nutrient properties of the malts, than determination of the permanently soluble nitrogen. Only a proportion of this nitrogen is assimilable by yeast but the total quantity appears to provide a satisfactory measure of the nutrient fractions. The best comparison for this purpose is obtained by expressing the permanently soluble nitrogen as a percentage on the wort solids. The latter were calculated for the accompanying tables from the specific gravity of the extract wort by means of the solution divisor 4. It is sometimes useful for rapid calculation to know that the percentage of dry solids in the extract wort is $\frac{3}{40}$ of the extract in brewers' pounds of the malt, assuming a solution divisor of 3.97.

Malts Nos. 1, 2 and 3 are shown by the P.S.N. on wort solids to be identical in yeast-nutrient properties, the lower modification of No. 3 reducing its P.S.N., despite its greater nitrogen

content. It is possible that the yeast nutrients in the less well modified malts are lower than the P.S.N. comparison suggests, since the percentage of formol-nitrogen in the permanently soluble nitrogen of such malts is rather less than with more fully modified samples. No. 4 stands apart from the other three and would be chosen, despite its lower extract, in preference to any of them, for beers of light gravity or for use with flakes, grits or sugars which yield no soluble nitrogen. Its higher colour and corresponding flavour would also be advantageous under such circumstances, though probably unsuitable for all malt pale ales of high gravity. Although more highly cured than Nos. 1 and 2, the diastatic activity of No. 4 is greater, corresponding with its higher nitrogen content.

The malts were all of excellent appearance and physical character, while the analyses are all so satisfactory that the prices might well be governed by the extracts. Actual market conditions, however, placed a moderate premium on Nos. 1 and 2.

(196) Mild Ale Malts.

The analyses in Table 61 are representative of five types of mild ale malt. The Scotch Plumage-Archer and the Spratt-Archer are both of very high quality and there is nothing in the analyses, apart from the colour, to show that they are not

TABLE 61.—MILD ALE MALTS

	Scotch Plumage- Archer (5)	Spratt- Archer (6)	Yorkshire Plumage (7)	Medium Plumage- Archer (8)	Coarse Plumage- Archer (9)
Moisture % ..	1.7	2.1	2.0	2.6	2.5
Extract lb. per 336 lb. ..	100.6	99.0	99.4	97.2	96.8
Colour 1-inch cell ..	6.5	6.0	7.0	8.0	7.5
Cold water extract % ..	19.1	18.7	17.7	17.8	17.5
Diastatic activity L° ..	32.0	35.0	32.0	31.0	33.0
[α] _D of wort solids ..	120.5	120.2	121.5	120.4	120.4
Extract on dry malt ..	102.3	101.1	101.4	99.8	99.3
Total N % ..	1.322	1.400	1.469	1.473	1.596
P.S.N. % ..	0.488	0.541	0.489	0.514	0.561
„ on total N ..	36.9	38.6	33.3	34.9	35.1
„ on wort solids ..	0.64	0.72	0.65	0.69	0.76
1000-corn dry weight, gr. ..	37.0	32.8	37.0	34.4	40.4
Calculated extract ..	102.1	100.9	101.6	100.0	100.0
Extract index ..	108.2	108.7	108.8	107.8	107.3

fine pale ale malts. The analyses are well balanced and the malts well modified. The difference in extract indices is typical of the varieties. 108.5 was used to calculate the extract of the Spratt-Archer and 108 was used for all the Plumage-Archers in the Table.

The Yorkshire Plumage malt might be considered rather under-modified by some brewers, though probably about correct in this respect for brewers using the Yorkshire stone square system of fermentation. Despite this, its extract index is high but this is typical of the variety and 109 has been used for calculating the extract. The analysis of No. 8 is quite satisfactory for malt from a medium quality Plumage-Archer barley, a good malt for draught mild ales. The same might be said of No. 9, though its appearance was not very prepossessing with large coarse corns. Its modification is not very full and its extract index on the low side but the analysis is quite good and well balanced, having regard to the barley and its nitrogen content.

(197) Defective Malts.

Two examples are given in Table 62 of variations in malt analysis resulting from different treatment of the same barley. Nos. 10 and 11 were made from a steely, prematurely ripened Spratt-Archer barley. No. 10 was hard-ended and definitely under-modified as shown by the cold water extract and permanently soluble nitrogen, but the extract obtained was quite satisfactory. The barley was hardly of malting quality, had a very high nitrogen content and great difficulty was experienced in obtaining a satisfactory modification of the proteins. The results shown in analysis No. 11 were obtained by extending the flooring period to 12 days, with the temperature kept low. It is still under-modified but could be used for draught mild ale.

The second pair represent malts from a moderately good quality Plumage-Archer barley. No. 12 is an example of analyses with which little fault could be found if the standard determinations only were made. The difference in the cold water extracts of the two malts would probably pass without comment, but determination of the permanently soluble nitrogens showed a distinct difference, which would be reflected in their brewing qualities. They were dried pale for use in carbonated bitter beers, for which No. 12 was not suitable if more than a very short life was required. No. 13 is a definitely better malt for that purpose. Its fuller modification has resulted also in a gain of 0.7 lb. in extract and a great improvement in yeast-nutrient properties, as judged from the permanently soluble nitrogen. No. 12 could be successfully used in blends for draught beer.

TABLE 62.—MALT ANALYSES SHOWING SOME DEFECT IN BARLEY OR MALT

	Prematurely ripened Spratt-Archer barley		Good quality Plumage-Archer barley	
	9 days 63°-64° (10)	12 days 60° (11)	(12)	(13)
Moisture %	1.5	1.7	2.0	2.3
Extract, lb. per 336 lbs. ..	95.5	95.4	97.1	97.5
Colour 1-inch cell	4.5	5.7	4.0	4.0
Cold water extract %	16.0	18.2	17.7	18.6
Diastatic activity L°	34.0	35.0	33.0	35.0
Extract on dry malt	97.0	97.1	99.1	99.8
Total N %	1.876	1.890	1.560	1.555
P.S.N. %	0.546	0.594	0.466	0.560
„ on total N	29.1	31.4	29.8	36.0
„ on wort solids	0.76	0.82	0.63	0.75
1000-corn dry weight, gr. ..	38.0	37.5	37.0	36.5
Calculated extract	97.0	96.7	99.6	99.6
Extract index	108.5	108.9	107.5	108.2

The great difference between these barleys was that the Spratt-Archer was so steely and its nitrogen content so high that satisfactory modification could not be obtained by ordinary malting methods, whereas the low modification of No. 12 was due to an inappropriate malting process. A fuller modification was required and easily obtained, as shown by No. 13.

(198) Other Two-rowed Malts.

TABLE 63.—TWO-ROWED MALTS FROM FOREIGN BARLEYS

	Moravian (14)	Chilean Chevallier (15)	Bohemian Hanna (16)
Moisture %	1.8	1.6	2.5
Extract lb. per 336 lb. ..	98.9	99.9	99.8
Colour 1-inch cell	6.5	6.5	4.0
Cold water extract %	17.1	18.7	20.2
Diastatic activity, L°	37.0	38.0	35.0
[α] _D of wort solids	119.8	117.4	120.0
Extract on dry malt	100.7	101.5	102.3
Total N %	1.518	1.480	1.520
P.S.N. %	0.562	0.618	0.600
„ on total N	36.9	41.8	39.5
„ on wort solids	0.75	0.82	0.79
1000-corn dry weight, gr. ..	35.2	33.6	35.0
Extract index	109.0	109.8	110.7

The three analyses in Table 63 are representative of European and Chilean two-rowed malts made in England. The cold water extract of the Moravian appears rather low in comparison with the permanently soluble nitrogen but the most striking feature in the analyses is the high extract index in each case. This shows that the barleys would all give a distinctly higher extract than English barleys of the same nitrogen content and thousand-corn weight and probably corresponds with their mellowness.

(199) English Six-rowed Malts.

There is apparently, as yet, no six-rowed variety of barley on which reliance can be placed in the English climate to yield good malting grain and satisfy the farmer's requirements. Under favourable conditions, however, certain six-rowed barleys suitable for malting and brewing can be grown and have physiological characters similar to those of imported barleys of the same type. This is shown ¹ for F 112 (see Fig. 18) in Table 64. In this instance the nitrogen content of the malts was not determined and the extract comparisons have been made with the barley analyses and the equation

$$E = A - 10.5 N + 0.2 G$$

TABLE 64.—ENGLISH-GROWN SIX-ROWED BARLEYS AND MALTS, F 112

			No. 17	No. 18
<i>Barley.</i>	Moisture %, kiln dried		12.4	13.9
	Nitrogen % on dry		1.366	1.295
	1000-corn dry weight, grams ..		35.8	37.6
<i>Malt.</i>	Moisture %		1.6	2.5
	Extract, lb. per 336 lb. (Seck $\frac{1}{2}$ mm.)		92.3	93.7
	(Seck 1 mm.)		88.8	91.6
	difference %		3.94	2.29
	Colour 1-inch cell		6.0	3.2
	Cold water extract %		16.1	16.6
	Diastatic activity, Lintner ° ..		23.0	35.0
Extract on dry malt			93.8	96.1
P.S.N. % on dry malt			0.386	0.404
,, on barley N.			28.3	31.2
,, on wort solids			0.55	0.56
Extract index			101.0	102.1

There is not sufficient information on this barley on which to base an average figure for A. The extract indices have consequently been calculated and compared with the average varietal

factor of 103 used for Californian barleys. The relation between permanently soluble nitrogen and total nitrogen and the deductions to be drawn from it are also, apparently, similar to those with Californian malts. The results show that the malts are of very similar character to Californians but probably more closely allied to Chilean (see Table 66).

The analyses provide a good example of the effects of varying modification with six-rowed malts. No. 17 is definitely less fully modified than No. 18. This is shown by the cold water extract, by the difference between the extracts of malts ground at Seek $\frac{1}{2}$ mm. and 1 mm. and by the permanently soluble percentage of the total nitrogen. On these grounds No. 18 would be preferred to No. 17 for most purposes. The extract index is rather lower than is usual with Californian malts and corresponds more closely with Chilean, Table 66.

(200) Californian Malts, English Made.

TABLE 65.—CALIFORNIAN MALTS, ENGLISH MADE

	Rather husky Coast type (19)	Atlas type		Stiff barley under- modified (22)	Very mellow hold-over barley (23)
		(20)	(21)		
Moisture % ..	1.9	1.7	2.0	1.8	2.0
Extract, lb. 336 lb. ..	91.9	94.0	94.1	92.8	94.4
Colour 1-inch cell ..	6.0	4.0	4.0	3.5	5.5
Cold water extract % ..	16.8	16.3	15.5	13.6	18.3
Diastatic activity, L° ..	31.0	33.0	25.0	25.0	30.0
[α] _D on wort solids ..	120.6	122.0	124.0	126.1	120.5
Extract on dry malt ..	93.7	95.6	96.0	94.5	96.3
Total N % " " ..	1.615	1.507	1.458	1.354	1.553
P.S.N. % " " ..	0.486	0.456	0.418	0.350	0.564
" on total N ..	30.1	30.2	28.7	25.8	36.3
" on wort solids ..	0.70	0.64	0.59	0.50	0.79
1000-corn dry wt., gr. ..	37.3	38.0	38.3	37.6	36.2
Calculated extract ..	94.1	95.4	96.0	96.9	94.5
Extract index ..	102.6	103.2	103.0	100.6	104.8

The analyses in Table 65 are typical of different types of Californian malt. No. 19 represents the more husky Coast type, Nos. 20 and 21 the whiter Atlas malts. The average varietal factor 103 was used to calculate the extracts and the extract indices obtained from the analytical figures correspond

with it very closely. The permanently soluble percentages of the total nitrogen of Nos. 19 and 20 are normal for English-made malts but No. 21 would generally be considered rather under-modified.

No. 19 would not be judged as inferior to No. 20 in brewing value. It represents a different type of malt, which might be preferred for some purposes on account of the greater quantity of husk and despite the two pounds lower extract, which is to be expected from this type of malt, particularly in view of its higher nitrogen content. Both analyses are well balanced.

Difference in brewing quality is more marked between Nos. 20 and 21, although they were made from the same type of barley and gave almost identical extracts. No. 21 is distinctly less fully modified, as shown by the lower cold water extract and permanently soluble nitrogen. It is typical of malt from a not uncommon type of Californian barley which appears to be deficient in enzymic activity and would in most cases be rejected in favour of No. 20. No. 22 is an example of poor quality Californian malt. Though the nitrogen content is low, it worked badly on the floor and resulted in a very under-modified malt with very low cold water extract and permanently soluble nitrogen but high $[\alpha]_D$. It will be noted also that the extract was $2\frac{1}{2}$ lb. lower than it should have been, giving an extract index of only 100.6.

No. 23 is such an unusual analysis for Californian malt that it is difficult to draw any conclusions from it. The barley had been held over and had become very mellow and kindly on the floor. The cold water extract of the ordinary standard analysis calls attention to this and would suggest the effects on the proteins which the extended analysis reveals. The cold water extract, permanently soluble nitrogen and its percentage on the total nitrogen resemble those of an English malt. The extract is also about two pounds higher than would normally be obtained from a Californian malt with the same nitrogen content. There was no question of forcing, either on the floor or kiln. The germination temperatures were low. The analysis provides an example of the fact that interpretation depends on comparison with others representing malts of known behaviour. This one is outside general experience but variation from the normal is not necessarily a sign of inferiority. Its meaning must be judged by brewing results, which are difficult to get when malts are used in blends. The figures, however, suggest that the malt would behave too much like an English, suitably to replace ordinary Californian. It might be supposed that its yeast-nutrient properties would be much superior to those of Nos. 20 and 22. In this respect, No. 22 is very definitely defective.

(201) Other Six-rowed Malts.

The analysis of Chilean in Table 66 is typical of a type of malt which some brewers find very satisfactory but others dislike on account of some loss of brilliance in the beers. The barley is frequently rather stiff and the difficulties encountered with the malts may be due to under-modification. Chileans generally please brewers who find a comparatively restricted modification advantageous. The example given is reasonably well modified. Californian Mariout barley is disliked by many on account of the difficulty experienced in obtaining satisfactory modification. The example given is a good analysis for this type of malt but shows signs of unkindliness in the somewhat low permanently soluble nitrogen and extract index. The high diastatic activity is typical of many Mariout malts. A varietal factor of 102 was used for calculating the extracts of these malts.

TABLE 66.—OTHER SIX-ROWED MALTS

	Chilean (24)	Californian Mariout (25)	Syrian (26)	Egyptian Mariout (27)
Moisture	2.0	2.2	2.4	1.8
Extract, lb. 336 lb.	93.1	90.1	90.6	86.2
Colour 1-inch cell	6.0	4.0	5.5	3.0
Cold water extract %	16.0	16.9	17.0	15.0
Diastatic activity, L°	33.0	50.0	31.0	37.0
[α] _D on wort solids	120.0	118.5	117.2	—
Extract on dry malt	95.0	92.2	92.9	87.8
Total N % „ „	1.518	1.621	1.430	1.689
P.S.N. % „ „	0.485	0.477	0.480	0.432
„ on total N	31.9	29.4	33.6	25.6
„ on wort solids	0.69	0.69	0.69	0.66
1000-corn dry weight, gr. ..	40.5	39.4	35.1	28.9
Calculated extract	94.9	93.5	92.6	88.5
Extract index	102.1	100.7	100.3	99.3

The Syrian was a fine tender malt of its type and the analysis represents it as well modified, with rather high cold water extract and permanently soluble nitrogen percentage on total nitrogen. The Egyptian Mariout was a very thin and rather hard malt, with low cold water extract and permanently soluble percentage of its total nitrogen. The extract obtained appears low but it is typical of the small and thin husky malts of the Mediterranean type. A varietal factor of 100 was used to calculate the extracts.

LAGER MALTS

(202) Manchuria-Oderbrucker Malts.

The analyses in Table 67 represent high-class malts made in America from Manchuria type barleys for use in lager beers. Wisconsin 38 is a smooth-awned barley from a cross between an Oderbrucker and a Russian barley. The extract given by these small berried malts is low, but the extract index calculated from the malt analyses is considerably higher than that obtained with English-made malts from six-rowed barleys of Mediterranean type and is comparable with that of English malts. It indicates that these malts give 2 to 5 lb. more extract than would be expected from Californian malts of similar nitrogen content and thousand-corn weight. They are examples of results obtainable from mellow barleys with very high nitrogen content.

TABLE 67.—AMERICAN MANCHURIA AND ODERBRUCKER BARLEYS AND LAGER MALTS (AMERICAN-MADE)

	Oder- brucker (28)	Manchuria (Minnesota) (29)	Wis- consin 38 (30)	Manchuria (N. Dakota) (31)
<i>Barleys.</i>				
Moisture %	14.5	12.2	11.8	13.2
N % on dry	2.138	2.287	2.381	2.315
1000-corn dry wt.	35.3	35.1	26.8	35.3
<i>Malts.</i>				
Moisture %	3.9	4.2	3.6	4.3
Extract lb. 336 lb.	87.2	86.2	83.3	86.6
Colour 1-inch cell	2.2	2.2	2.0	1.8
Cold water extract %	16.4	17.8	17.3	16.8
Diastatic activity, L°	91.0	94.0	170.0	93.0
Extract on dry malt	90.7	90.0	86.4	90.5
Total N % " "	2.061	2.338	2.367	2.282
P.S.N. % " "	0.565	0.681	0.682	0.562
" on total N	27.4	29.1	28.8	24.7
" on wort solids	0.84	1.02	1.06	0.83
1000-corn dry weight, gr. ..	31.7	32.2	24.7	32.7
Extract index	104.6	107.7	106.0	107.5

The appearance and high nitrogen content of these small berried malts do not recommend them to English brewers, but they are fine material for lager beer or carbonated ales made by the American methods with high percentages of unmalted grain. Under these conditions they give beers that retain their brilliance

for long periods after pasteurisation. The high percentage of permanently soluble nitrogen on wort solids will be noted although its percentage on total nitrogen is similar to that of Californian. This should make them useful in blends with low nitrogen malts, particularly for light gravity ales.

(203) European Lager Malts.

Pale and dark lager malts are commonly described as of Pilsen and Munich type respectively. Typical analyses of these are given in Table 68, with an English-made pale lager malt. The very low colour of the Pilsen malts, corresponding with about 2.0 on the Tintometer scale in a 1-inch cell, and the high diastatic activity, equivalent to between 60° and 85° Lintner, are noticeable. The Munich malts have colours of 7-10 on the Tintometer scale, with a diastatic activity of about 30° Lintner. The comparatively high nitrogen content of the Continental lager malts is also characteristic. The extract indices are calculated from an equation involving protein content, since this is more commonly used than nitrogen percentage in Continental analyses. This equation is

$$E = A - 0.85 P + 0.15 G$$

TABLE 68.—LAGER MALTS

	Pilsen (32)	Munich (33)	Danish		English (36)
			Pilsener Spratt- Archer (34)	Munich Binder (35)	
Moisture %	6.1	4.2	3.8	2.1	3.5
Extract % Plato dry,					
Fine	78.0	77.0	79.7	79.2	82.6
" " Coarse	—	—	78.7	78.2	82.0
Colour (Brand) ..	0.16-0.18	0.7-0.9	0.21	0.6	0.17-0.19
Diastatic activity W-K	300	90	200	110	230
Protein % on dry ..	11.36	11.40	10.1	11.1	8.94
" soluble % "	4.24	3.76	—	—	—
" perm. sol. % "	—	—	3.8	4.0	3.59
Sol. protein % of total	37.3	33.0	—	—	—
Perm. sol. protein "	—	—	37.5	36.0	40.2
1000-corn dry wt., gr.	32.2	33.0	33.8	37.5	35.7
Calculated extract ..	78.2	78.2	79.5	79.4	80.8
Extract index ..	82.8	81.8	83.2	83.0	84.8

An average value of 88 has been found for A with normally modified Continental lager malts and this has been used for

the calculated extracts in the table. The difference between the latter and the extract found or the extract index suggests that the modification of No. 33 was lower than that of the other malts. Lager malts are usually less fully modified than ale malts. This is reflected in the soluble protein percentages of 37.3 and 33 on the total protein. These are more often given than permanently soluble protein in Continental analyses and may be about 5% higher than the latter. The Danish malts, for which permanently soluble protein is given, are more fully modified and more suitable for use with grits.

The following figures were given by Kolbach² for the percentage of soluble protein extracted in the Congress wort on the total nitrogen of the malt in relation with the modification of lager malts.

Very well modified malts	..	41-
Well modified malts	..	36-41
Moderate modification	..	35 or less

The permanently soluble percentage of the total nitrogen and the extract index of the English-made lager malt are unusually high, but are typical of the very ready modification of the English barleys of 1936. The nitrogen content was 1.430% on dry malt, giving an extract index of 110.5 when calculated by the equation used for English malts from an extract of 103.2 lb. on dry basis. The figures for all these malts in English units are given in Table 69.

TABLE 69.—EXTRACT FIGURES FOR LAGER MALTS

	Pilsen (32)	Munich (33)	Danish		English (36)
			Pilsener Spratt- Archer (34)	Munich Binder (35)	
Extract lb. per qr. dry	97.5	96.3	99.6	99.0	103.2
Nitrogen % on dry malt	1.817	1.824	1.616	1.776	1.430
Extract index ..	109.7	108.4	109.3	109.6	110.5
P.S.N. % on wort solids	—	—	0.82	0.87	0.75

(204) Lager Malts, Congress and Institute Analyses.

Analyses of two pale lager malts are given in Table 70 to show the relation between results obtained by the Congress and Institute of Brewing methods.

TABLE 70.—LAGER MALTS, CONGRESS AND INSTITUTE ANALYSES

	French		Danish	
	Congress	Institute	Congress	Institute
Moisture %	2.4	2.2	6.0	5.7
Extract, fine grind and Seck 0.5 mm. on dry	79.0	97.6	78.1	97.1
Colour	0.36-0.38	4.5	0.24-0.26	3.0
Cold water extract %	—	17.4	—	16.0
Diastase, Windisch-Kolbach and Lintner	91	26	194	58
Saccharification time	10-15 min.	—	less than 10 min.	—
Odour	normal	—	mildly aromatic	—
Filtration	bright	—	bright	—
Total protein or N % dry ..	9.30	1.488	12.35	1.976
P.S. Protein or P.S.N. % dry ..	3.26	0.424	3.94	0.506
„ % on total protein or N ..	35.1	28.5	31.8	25.6
„ % on wort solids	3.21	0.58	3.94	0.70
1000-corn dry weight, grams ..	29.8	29.8	36.9	36.9
Extract index	82.5	106.8	83.1	109.9

The permanently soluble nitrogen of the small French malt indicates only a moderate modification for lager malt, while that of the Danish malt indicates definitely lower modification than is usual. This would be expected from such a high total nitrogen content. The colour of the French malt is higher than that of typical Pilsen malt and its diastatic activity rather low. They correspond more closely with malt of Dortmund type.

SELECTION OF MALT ON ANALYSIS

(205) Analytical Criteria.

Requirements are so varied for different kinds of beer that the results of malt analyses must be judged by comparison with those obtained with other malts of the same type which experience has shown to be suitable for the purpose intended. The figures may in some cases fail as reliable criteria of the quality of malt and should always be supplemented by physical appreciation of its soundness, tenderness and flavour, having regard to its type. With the assurance that the samples are free from obvious physical defects arising either from the original barley or unsatisfactory malting, the analytical figures should be critically

examined in the manner explained in previous chapters to make sure that they are well balanced and correspond with the degree of modification required.

It is only after satisfaction has been obtained in regard to the type, colour, flavour, modification and the general balance of the analytical results that consideration should be given to the extract and yeast-nutrient properties of the malt, since, however good these essential characters are, they do not in themselves prove that the malt would be a satisfactory brewing material. The extract should be as high as possible consistent with the type and nitrogen content of the malt, in which connection it will be borne in mind that excessive growth and modification lead to a loss of extract as well as inadequate growth, and that extract can also be reduced by the production of steely corns on the kiln.

The permanently soluble nitrogen percentage of the wort solids provides, at present, the best criterion of yeast-nutrient properties. The percentage obtained in brewery wort is considerably higher than that in the laboratory extract wort, on account of greater proteolysis in the thicker brewery mash. It is not at all an easy matter to obtain this relationship in practice but it should be determined if opportunity arises in order to provide another means of interpreting the ordinary analytical figures, which must normally be used as the basis of comparison. Oliver³ found an increase averaging 33% and 36% in the permanently soluble nitrogen of experimental thick mashes over that in the extract mash with English and foreign malts and came to the conclusion that factors other than concentration were concerned in this increase, which was not regular. Other observations have indicated that the increase is much less, approximating more closely to 10%.

The minimum requirements of yeast in regard to wort nitrogen are not known but it is obvious that the quantity present in a given volume of wort of low gravity is considerably less than in the wort for a stronger beer from the same malt, but the quantity of yeast and therefore, presumably, the nitrogen assimilation, produced in the brewery is not proportional with the gravity or nitrogen content of the wort. There is consequently no direct relation between the wort nitrogen required and the P.S.N. of the malt most suitable for beer of different gravities, but it is clear that a malt with a higher P.S.N. is desirable for low gravity beers in comparison with those of higher gravity. This point should be decisive in selecting appropriate malts for different beers. Thus, if the low nitrogen malts Nos. 1 and 2 were found to be most suitable for pale beers of fairly high gravity, it is

probable that there would be some lack of yeast nutrients in low gravity worts from the same malts, for which Nos. 3 and 4 might prove better. No definite guide to the correct relation between the permanently soluble nitrogen of the wort solids in malt analysis and the gravity of the brewery worts can be given. It no doubt varies in different breweries and must be considered in relation with the percentage of malt adjuncts used, but there can be little doubt that a more or less definite minimum quantity is required to prevent yeast starvation, a very important consideration in the selection of malts. Bishop⁴ suggested the figures given in Table 71 for "wort nitrogen," P.S.N. as % of wort solids, required in worts for beers of the original gravities given. These figures have no claim to be more than a suggestion which might be followed up in the brewery, but they emphasise that malts with higher nitrogen content should be selected for lower gravity beers, a requirement that is not always easy to meet, as quality and modification generally fall with increasing nitrogen content.

TABLE 71.—WORT NITROGEN REQUIREMENTS AT DIFFERENT GRAVITIES

Beer. Original gravity	Wort nitrogen required, P.S.N. % on wort solids
-1080	0.65
1079-1060	0.70
1059-1050	0.75
1049-1040	0.80
1039-1030	0.85
1029-	0.90

(206) A suggested Basis of Classification for Malts.

Since the permanently soluble nitrogen of normally modified malt of given variety bears a definite relation to the extract of the malt, it is possible to classify malts according to their extracts in groups that should give the wort nitrogen required for beers of different gravity. Bishop further suggested a classification of this kind (Table 72). The extracts given are on sample, not on dry malts, so that malts with higher moisture content would be automatically degraded. In view of the general practice of using a proportion of foreign six-rowed malts with English malts, the Table includes an indication of those appropriate for beers of the different gravities. Six-rowed malts of Californian type compared with English yield only about 5/6 as much wort nitrogen for equal nitrogen content and therefore act as nitrogen diluents and, on that account, may not always be suitable for the low

gravity beers. It is suggested that malts from barleys of Manchuria type, which give a higher wort nitrogen if malted similarly, might be more useful for those beers.

TABLE 72.—CLASSIFICATION OF MALTS ON THE BASIS OF EXTRACT AND USE

	British and other two-rowed malts Extract on sample	Approximate assignment to beer gravity	Six-rowed malts used to adjust wort nitrogen Extract on sample
Class 1	-100.5	-1080	<i>Calif., Chilean, etc.</i>
„ 2	100.4-99.5	1079-1060	Class A -93
„ 3	99.4-98.5	1059-1050	Class B 92.9-91
			Class C 90.9-89
			Class D 88.9-87
Class 4	98.4-97.5	1049-1040	<i>Manchuria.</i>
„ 5	97.4-96.5	1037-1030	Class A -93
„ 6	96.4-95.5	1029-	Class B 92.9-91
			Class C 90.9-89
			Class D 88.9-87

Approximate figures for the relationships between extract, nitrogen content, P.S.N. %, wort solids %, and P.S.N. as % of wort solids, all on dry basis, for English and Californian malts are given in Table 73. The P.S.N. is taken as 36 and 30% of the total nitrogen in the respective malts and the wort solids as 3/40 of the extract. Values of 108.5 and 103 are taken for A and 36 grams for the 1000-corn dry weight.

TABLE 73.—RELATION BETWEEN EXTRACT, NITROGEN AND WORT SOLIDS IN ENGLISH AND CALIFORNIAN MALTS

<i>English Malts.</i>							
Extract, lb. dry malt ..	102	101	100	99	98	97	96
Nitrogen % „ ..	1.36	1.45	1.55	1.64	1.74	1.83	1.92
P.S.N. % „ ..	0.49	0.52	0.56	0.59	0.63	0.66	0.69
Wort solids % „ ..	7.65	7.58	7.50	7.43	7.35	7.28	7.20
P.S.N. % on wort solids	0.64	0.69	0.74	0.79	0.85	0.90	0.96
<i>Californian Malts.</i>							
Extract, lb. dry malt ..	98	97	96	95	94	93	92
Nitrogen % „ ..	1.22	1.31	1.41	1.50	1.59	1.69	1.80
P.S.N. % „ ..	0.37	0.39	0.42	0.45	0.48	0.51	0.54
Wort solids % „ ..	7.35	7.28	7.20	7.13	7.05	6.98	6.90
P.S.N. % on wort solids	0.50	0.54	0.58	0.63	0.68	0.73	0.78

(207) Summary.

For fullest interpretation of the results of a commercial analysis of malt, it is necessary to determine the nitrogen content,

permanently soluble nitrogen of the extract mash and thousand-corn weight, in addition to the estimations included in the standard schemes. The extract can be related to the nitrogen content by the following formula, in which A is called the extract index and should be about 108·5 for English malts and about 103 for Californian six-rowed and similar malts in a normal season.

$$E = A - 10\cdot6N + 0\cdot22G$$

The permanently soluble nitrogen when expressed as a percentage of the total nitrogen of the malt gives a good idea of the degree of modification, 36% being a good figure for normally modified English malts and 30% for Californian. Though these figures are given as a kind of datum line, the percentage most suitable under the conditions in any particular brewery or for the type of beer brewed must be determined by experience. It should indicate the most desirable balance of desirable and undesirable properties, and would then provide a criterion of the utility of the malt.

Every malt analysis should be judged on this basis to ensure that malt modification has been carried sufficiently far to assure the necessary degree of protein stability in the beer and not so far that reduction in fulness or head-retaining properties should result. An adequate quantity of yeast-nutrient nitrogen in the wort should be assured by consideration of the "wort nitrogen" or percentage of permanently soluble nitrogen on the wort solids. The percentage required for low gravity beers is greater than for stronger beers and the necessary allowance must be made to counterbalance the lack of soluble nitrogen in adjuncts. No definite guide can be given for the quantity of permanently soluble nitrogen required in malts for different beers, which will vary with brewing conditions. A malt containing 1·3 to 1·4% of nitrogen is usually satisfactory for the stronger beers, but 1·5% or more is generally desirable with 15 to 20% of malt adjuncts.

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CHAPTER XIII

SPECIAL MALTS AND UNMALTED CEREALS

(208) Use of Special Malts.

The properties of flavour, colour, enzymic activity, extent of enzymic change and acidity developed during germination and kilning are so inter-dependent in malts made by ordinary methods that it is impossible to emphasise one to any marked degree without limitation of others. They depend ultimately on the characteristics of the barley, the power of the maltster to control the changes during malting being somewhat circumscribed. This is apparent in the comparatively small differences in pale and dark malts made from similar barleys. They can be varied sufficiently to cover the requirements for many kinds of beer, but not for all the types required, and it is necessary to bridge the differences in flavour between pale beers and stouts by the use of highly flavoured and coloured roasted malts and barleys or by the employment of a proportion of unmalted grain, sugars or caramel. With these it is possible to produce a wide range of beer types by variation in the proportions used with grists consisting mainly of ordinary malts to supply the properties partly or completely suppressed in the special malts or lacking in the other adjuncts. Other malts are available in which enzymic activity, protein modification and with it, presumably, changes in other malt constituents or acidity have been emphasised. The importance now attached to the acidity of malt and its influence on enzymic changes in the mash tun and on the physical behaviour of protein and other wort constituents partly explains the value of Dixon's Enzymic malt, in which this property has been developed to a high degree in the course of manufacture. It not only supplies any lack in this respect and helps to counter-balance the enzyme-restricting influence of carbonate liquors but contributes fully degraded yeast-nutrient substances produced during malting by the stimulating effect of the acid. It is also possible, by special malting processes, to increase colour and flavour without undue restriction of enzymic activity and, thereby, produce such a malt as Diamber for use in dark beers, which particularly depend on these characters.

Malt extract may, in addition, be considered with the malts,

rather than in connection with sugar syrups, which it physically resembles more closely. It is a product in which certain of the properties of green malt, normally weakened on the kiln, can be retained to a considerable extent and made available in convenient form. Though undoubtedly a useful adjunct to malt, the reasons for its use are but vaguely known. They are generally attributed to its high enzymic activity, which can be readily demonstrated in respect of diastatic power and with less definiteness for other enzymes, but there can be no doubt that other factors operate. The far-reaching digestion during mashing of very low dried malt at comparatively low temperatures results in the production of unusually high proportions of degradation products of many kinds, among which low molecular nitrogenous substances and inorganic phosphates are best known. They constitute buffer mixtures which probably help to stabilise conditions in the brewery mash and tend to counterbalance unexpected irregularities in the grist, as well as supply constituents that may be lacking in the ordinary malt.

Though barley must remain the chief raw material of brewing, malted wheat and oats possess special properties which make a small quantity useful in some grists. With such a wide range of roasted and special malts available, it is possible very greatly to vary the composition of wort and the character of beers. Their proper selection and use consequently becomes of great importance in making up the grist and will be dealt with in a later chapter.

(209) Colour and Aroma of Malts—Melanoidins.

When certain sugars are heated in strong solution with amines, amino-acids or polypeptides under suitable conditions, they form coloured, aromatic, colloidal condensation products which are usually referred to under the name of Melanoidins, given to them many years ago by their discoverer, Maillard. There are considerable differences in the rate at which sugars react in this way with amino-acids. The pentoses, xylose and arabinose, react almost instantaneously; glucose, fructose, galactose and mannose fairly rapidly; maltose and lactose slowly, while the reaction with cane sugar requires several hours and probably takes place only after inversion. The higher polysaccharides do not appear to form condensation products of the melanoidin type.

The rate of reaction varies also with the nature of the nitrogenous compound and with such conditions as temperature, pressure and concentration. Amines react very rapidly and develop colour with sugars almost instantaneously. The amino-

acids come next in speed of reaction, while the polypeptides require one to two hours to develop colour when heated with glucose solution. The colour and aroma of the condensation products also vary considerably with different amino-acids. Glycocoll develops colour rapidly, but the aroma produced is weak and similar to that of caramel. Valine reacts slowly, with development of a fine aroma of roasted malt. Leucine reacts very slowly and has a low colouring power, giving a product with an aroma of malt. Asparagine and glutamic acid react only slowly and slightly. These reactions can be verified by heating mixed solutions in test tubes.

The condensation products all have an acid reaction and belong to the group of hydrophilic colloids, giving solutions with high viscosity. They can exist in two forms; one soluble and reversible, the other insoluble and irreversible. A water-soluble product is formed by precipitation with such salts as zinc sulphate and ammonium sulphate, while electrolytes precipitate insoluble products. With increasing concentration the melanoidins all become more insoluble and the dry substances are almost insoluble in water. Their aromas also decrease with the solubility, and high temperatures destroy their most important properties, colour and aroma. Excess of glucose retards the speed at which they become insoluble. The colloidal character of melanoidins is shown by fluorescence of their solutions and formation of a fairly stable foam when these are shaken with air.

(210) Colour and Aroma of Malt.

The colour and aroma of ordinary malts is attributed in large measure to the production of melanoidins by condensation of sugars and nitrogenous substances on the kiln, after the temperature has been reached at which enzymic activity is arrested. Hence the importance of the manner in which the earlier stages of drying are carried out. Rapid drying at low temperatures, with abundance of draught, is necessary with pale malts to prevent enzymic action and the production of sugars, which would increase the formation of aromatic, colouring substances when the higher temperatures are reached. It is necessary, on the other hand, to encourage the production of enzymic breakdown products in dark malts, and that in proportion with the aroma and colour required. Hence the higher temperatures while the moisture content is still high. (Sections 147 and 158.) If the proper moisture and temperature conditions for the formation of the necessary carbohydrate and protein breakdown products and their condensation do not exist, no aromatic substances would be formed on the kiln and the dark coloured products

of torrefaction would be produced instead when the temperature became sufficiently high, as is the case in malt roasting. Similar reactions between sugars and nitrogenous substances occur during mashing and boiling but with much less intensity than on the malt kiln or in the manufacture of caramel with ammonium salts.

COLOURED MALTS

(211) Roasted Malts.

Various kinds of roasted malt are differentiated by the names black or patent, brown, amber and crystal, to which might be added roasted barley, which is very similar to, though rather different in flavour and colloidal properties from black malt. It is dryer and not so smooth or rich in flavour as black malt, for which reason it is preferred in some stouts, contributing to the firmness and whiteness of the head. These malts are also used, in smaller proportions, in dark ales, not only for their colour but also on account of their characteristic flavours. These have distinct effects on the flavour of the stout or ale, even when used in comparatively small proportions, so that considerable care is required to find the most satisfactory blend in grists. The flavour given by amber and crystal malts is much appreciated in many ales and stouts. Brown malt is less used, and is intermediate in flavour and colour between black and amber or crystal. The question of flavour is so important that these malts should always be used freshly roasted, as is the case with coffee, which good black malt closely resembles. The aroma disappears rather quickly during storage, particularly if the malt becomes slack.

(212) Black Malt.

Black malt is made from kilned malt, which has been germinated for 7 or 8 days, by roasting in a revolving cylinder, generally over gas jets. It is essential that germination should have been regular, otherwise an evenly roasted product is not obtained. Unmaltered corns require longer exposure to heat, so that fully grown corns would be over-roasted or converted to insoluble carbon before partly grown or ungrown corns were finished. Well-made black malt should contain few, if any, carbonised corns, but 10 to 15% of insoluble carbon may be found in defective samples. The temperature of caramelisation is, according

to Valentine,¹ round about 445° Fahr. and that of carbonisation about 480° Fahr. Hence the care necessary in manufacture.

TABLE 74.—ANALYSES OF BLACK MALTS AND BARLEY

	English malts		Six-rowed malt	Roasted barley
	1	2		
Moisture, %	1.5	2.9	2.5	3.0
Extract lb. per 336 lb.	91.5	80.1	76.6	84.0
Colour, 10% extract 1-in. cell ..	1470	1500	1200	1200

Table 75 was given by Hulton and Ward² for the relation in colouring power between black malt and caramel. It represents to the nearest bushel the number of quarters of black malt on the measure basis according to which it is frequently sold, an average value of 264 lb. being taken for one quarter, which would be required to give the same colour as caramel, also expressed in quarters of 224 lb.

TABLE 75.—NUMBER OF QUARTERS (264 LB.) OF BLACK MALT EQUIVALENT TO 1 QUARTER CARAMEL (224 LB.)

Colour of malt AV. % CARAMEL 1-inch cell	Actual colour of caramel						
	20,000	25,000	30,000	35,000	40,000	45,000	50,000
800	21 $\frac{3}{8}$	25 $\frac{5}{8}$	31 $\frac{3}{8}$	35 $\frac{5}{8}$	41 $\frac{3}{4}$	44 $\frac{3}{4}$	51 $\frac{1}{4}$
900	18 $\frac{7}{8}$	23 $\frac{3}{8}$	27 $\frac{7}{8}$	31 $\frac{1}{4}$	34 $\frac{3}{4}$	41 $\frac{1}{4}$	43 $\frac{3}{4}$
1000	15 $\frac{1}{4}$	21 $\frac{1}{8}$	24 $\frac{1}{2}$	3	3 $\frac{3}{8}$	33 $\frac{3}{4}$	41 $\frac{1}{4}$
1100	13 $\frac{1}{2}$	17 $\frac{7}{8}$	21 $\frac{1}{4}$	23 $\frac{3}{4}$	3	31 $\frac{1}{2}$	37 $\frac{7}{8}$
1200	13 $\frac{3}{8}$	15 $\frac{3}{4}$	21 $\frac{1}{8}$	23 $\frac{3}{8}$	24 $\frac{3}{4}$	31 $\frac{1}{8}$	31 $\frac{1}{2}$
1300	11 $\frac{1}{4}$	15 $\frac{3}{8}$	2	21 $\frac{1}{4}$	23 $\frac{3}{8}$	27 $\frac{3}{8}$	31 $\frac{1}{4}$
1400	11 $\frac{1}{4}$	11 $\frac{3}{8}$	17 $\frac{7}{8}$	21 $\frac{1}{8}$	21 $\frac{3}{8}$	24 $\frac{3}{4}$	3
1600	11 $\frac{1}{8}$	13 $\frac{3}{8}$	13 $\frac{3}{4}$	2	21 $\frac{1}{4}$	23 $\frac{3}{8}$	27 $\frac{7}{8}$

(213) Brown and Amber Malts.

Brown and amber malts are finished either on the kiln or in a roasting cylinder and, in the former case, sometimes over brightly burning oak battens which contribute a rather empyreumatic flavour. It is generally considered that kiln amber has a better flavour than cylinder amber. Diastatic activity is destroyed in brown malt but may be retained to a slight extent by amber malt. Analyses are given in Table 76.

TABLE 76.—ANALYSES OF BROWN AND AMBER MALTS

	Brown malts		Amber malts				
	1	2	1	2	3	wheat	pale
Moisture %	1.2	2.4	2.5	2.8	1.2	2.6	2.0
Extract lb. per 336 lb. ..	90.6	87.8	88.4	87.0	92.5	103.0	96.4
Colour 10% extract 1" cell	102	212	62	120	102	24	10

(214) Crystal or Caramel Malt.

Crystal malt differs from the previously described roasted malts in that green instead of dried malt is roasted in the revolving cylinders. On the Continent it is usually known as caramel malt and may, alternatively, be made from kilned malt which is sprinkled or steeped before roasting. The manufacturing process consists essentially in heating the green or wetted malt at first between 150° and 170° Fahr., when the contents of the corns liquefy and what is practically a mashing process occurs. As the temperature gradually rises, the malt is dried and the roasting stage of the process supervenes, the whole taking 2 or 3 hours. When the malt is discharged from the cylinders, the endosperms are liquid but gradually set to a crystalline mass on cooling. This mass should be of a uniform brown colour. The changes in the corns are quite different from those occurring in other roasted malts on account of the presence of water. The liquefaction and saccharification of starch in the kernels is far in excess of that in ordinary malts, so that the reducing sugars calculated as maltose may account for 30–50% of the dry matter.

TABLE 77.—ANALYSES OF CRYSTAL MALTS

	1	2	3	4	Caramel malt
Moisture %	4.0	4.0	4.2	4.3	5.0
Extract, lb. per 336 lb. ..	86.3	90.5	84.4	84.5	82.5
Colour, 10% extract 1" cell	85	120	150	190	85

The conditions existing in the malt corns at the lower temperatures in the cylinder bear some relation to those of mashing, though the relative proportions of water and solid matter are very different. The ratio of malt to water is about 1 : 0.64 and the concentration of starch conversion products becomes so high that transformation is greatly restricted. Kolbach and Schild⁸ found that the optimum temperature for maltose formation under

conditions of this kind was between 149° and 158° Fahr. as compared with 145°–147° in the mash tun. They concluded that proteolytic activity was not retarded nearly to the same extent by the low water to malt ratio, but the physico-chemical coagulation of proteins was much greater. The production of soluble and formol nitrogen was found to be little less than in mashing, if the saccharification temperature was kept about 140° Fahr., but higher temperatures were more favourable to starch conversion.

(215) Analysis of Coloured Malts.

Although roasted malts are commonly purchased in England on a measure basis and in Ireland at 252 lb. (9 stones) per quarter, the Institute of Brewing standard methods of analysis for coloured malts⁴ recommend that all analytical results should be expressed on the standard quarter of 336 lb. Brown, Crystal and Amber malts are mashed in the presence of diastase, in the form of a known volume of cold water malt extract, and a control is carried out to correct for the specific gravity of the latter. Otherwise the determination of extract is similar to that laid down for ordinary malts. Black barley and malt are extracted by boiling water for 1 hour and the volume made up to 515 ml. In both cases the extract is calculated from $(\text{sp.gr.} - 1000) \times 3.36$ and reported as Brewers' pounds per quarter of 336 lb., or, if preferred, in degrees per quarter.

The colours are determined by diluting the extract worts to such an extent that they can be measured in the Tintometer against the 52 series standard glasses. For comparative purposes the colours found are calculated to a 10% wort basis, to correspond with other malts. Brown and crystal malts are diluted 5 times and the colour read in the $\frac{1}{2}$ -inch cell, the reading being multiplied by 10 to give the colour of a 10% extract in a 1-inch cell. Roasted barley and malt extracts are diluted 50 times and the colour determined in the $\frac{1}{2}$ -inch cell. The result multiplied by 100 gives the colour of a 10% extract in a 1-inch cell. The extract and colour of roasted malts varies considerably with the kind of malt used and the degree of roasting to which it has been subjected. A higher colour generally means a lower extract with comparable raw material.

SPECIAL MALTS

(216) Dixon's Enzymic Malt.

According to Dixon's original patent, the steeped barley is allowed to germinate for about 3 days on the floor in the ordinary

manner. It is then sprinkled with a 10% solution of lactic acid at the rate of 3 gallons per quarter and germination allowed to continue for another two days, when the grain is again sprinkled as before, kept at a temperature of 80° Fahr. for 24 hours, and steeped in a 20% lactic acid solution for one day at 60° Fahr. The malt is then kiln-dried.

The process actually employed is varied from this as required to produce malts of different types. In particular, chemically prepared lactic acid is not used. The sprinkling and steeping liquors are prepared by biological souring of a mash, in a manner similar to that described for the biological acidification of a brewery mash in Vol. II. The process is thus an entirely natural one and results in the activation of enzymic processes during germination, particularly proteolytic breakdown. The analysis given in Table 78 shows that the permanently soluble nitrogen may be increased from the normal 36% to 50 or 60% of the total nitrogen. In addition, the nitrogenous substances contributing to this high percentage of permanently soluble nitrogen are of a simpler type than in ordinary malt, amino-nitrogen accounting for 50 or 60% of it. To this is attributed the benefit to yeast nutrition noticed when a small percentage of the malt is used in a grist. Enzymic malt is more especially used to increase the acidity of wort in the manner and with results described in the sections on controlling the reactions of mash and wort.

TABLE 78.—ANALYSIS OF DIXON'S ENZYMIC MALT

Moisture per cent.	4.6
Extract lb. per 336 lb.	94.0
Colour, 1-in. cell	8.0
Cold water extract %	28.7
Diastatic activity L. ^o	30.0
[α] _D of wort solids	113.9
Extract on dry malt	98.5
Total nitrogen % on dry malt	1.592
P.S.N. % on dry malt	0.954
„ % on total nitrogen	60.0
„ % on wort solids	1.10
Formol-N. % P.S.N.	60.0
1000-corn weight	32.1
Acid as lactic acid % on dry malt	2 to 2.5

(217) Diamber Malt.

This name has been given to a malt made in England by a flooring process that differs in several respects from that practised with other types of malt, particularly with regard to temperatures

at certain periods. The result is a fully germinated and normally kilned malt of very high colour but with ample diastatic activity to complete the conversion quite readily and yield a brilliant wort of deep colour and fine aroma. As a rule it is blended with ordinary malts, but in higher proportion than is possible with crystal malt. It is useful in dark ales or lagers, 5 to 10% in the grist increasing their fulness of flavour. An analysis is given in Table 79.

TABLE 79.—ANALYSIS OF DIAMBER MALT

Moisture %	1.5
Extract lb. per 336 lb.	95.0
Colour 10% wort 1-in. cell	17.5
Cold water extract %	19.3
Diastatic activity, Lintner°	26.0
[α] _D of wort solids	122.8
Extract on dry malt	96.4
Total nitrogen % on dry malt	1.642
Permanently Soluble Nitrogen % on dry malt	0.532
“ “ “ % of nitrogen	32.4
“ “ “ % on wort solids	0.71
1000-corn dry weight, grams	34.9
Extract index	106.1

(218) Wheat Malt.

TABLE 80.—ANALYSES OF WHEAT MALTS AND OAT MALT

	1	2	3	Oat Malt
Moisture %	3.5	3.0	1.9	2.3
Extract lb. per 336 lb.	98.7	104.1	102.6	69.9
Colour, 10% wort, 1-inch cell	6.5	6.0	10.5	4.5
Cold water extract %	13.9	15.0	16.7	14.0
Diastatic activity	41.0	49.0	54.0	21.0
[α] _D of extract wort solids	126.9	123.7	120.4	—
Extract on dry malt, lb. per 336 lb.	102.3	107.3	104.6	71.5
Total Nitrogen % on dry	1.929	1.580	1.691	2.050
Permanently Soluble Nitrogen %	0.554	0.531	0.606	0.494
“ “ “ on N	28.7	33.6	35.9	24.1
“ “ “ wort solids	0.76	0.66	0.75	0.95
1000-corn dry weight	35.8	38.0	35.0	28.6
Extract index	114.9	115.7	114.8	86.9

Wheat malt is used in the production of some special types of beer, such as the Berlin Weiss beer, in which it may constitute 75% of the grist, but only to a very limited extent in ordinary beers. This is probably mainly due to the difficulty experienced in malting the naked grain without damage to the exposed acro-

spire and growth of mould. As a result much of the wheat malt made has been under-modified and produced turbidity and instability in beers in which it was used. Actually 5 or 10% of well-modified wheat malt can be employed in grists with ordinary malts, with advantage to the fulness and head-retaining properties of the beer, but adequate protein breakdown during malting is essential. Typical analyses of wheat malts are given in Table 80. Of these No. 1 has an excessive nitrogen content and must be considered as insufficiently modified.

(219) Malted Oats and Rye.

Malted oats are used to a certain extent, blended with barley malt, in some stouts but malted rye is not used in this country for brewing. Unmalted rye is useful for vinegar brewing and distilling on account of the liquefying power of its diastase. Baker and Hulton⁵ found that aqueous extracts of unmalted oats had a solvent action on oat starch, producing glucose, and that the amylase extracted from unmalted rye had a considerable liquefying activity.⁶ Precipitated diastase from unmalted barley and rye both carry the conversion of soluble starch to a resting point at which the reducing power is represented by R 60–65, the products being 60% crystalline maltose and 40% α -amylo-dextrin. The precipitated diastase from oats acts differently. It is able to convert practically the whole of the starch to maltose, if used in quantity equivalent to that derived from $2\frac{1}{2}$ to 5 times the weight of oats to unit weight of starch. A dextrin with the constants $R_{3.93}$ 9.3 and $[\alpha]_{D3.93}$ 185.9, together with a small quantity of a substance soluble in alcohol and having the properties ascribed to a malto-dextrin, and maltose were separated from a soluble starch conversion with the amylase of malted oats. The precipitated amylase of malted rye converts soluble starch in a manner similar to that of malted barley but the only products found were crystalline maltose and a dextrin of $[\alpha]_D$ 181.9 and R 11.4. An analysis of malted oats is given in Table 80.

(220) Malt Extract.

Malt extracts are highly concentrated syrups produced by concentration in vacuum pans of worts from very lightly cured malts. Various types are made for pharmaceutical purposes and for use in the baking, laundry and other industries as well as for brewing. The most distinctive character of most of these is their high diastatic activity, which depends on the type of barley selected, the malting methods, together with the mashing and concentration processes, and may be as high as 350° Lintner.

The malt is very low dried so that it retains substantially the enzymic activity of green malt, while the temperatures during mashing and concentration are not allowed to exceed 130° Fahr. Mashing temperatures between 120° and 130° Fahr. favour proteolytic digestion, so that it is possible to obtain malt extracts which contain a high percentage of permanently soluble and formol nitrogen. Typical analyses of the types of malt extract used in brewing are given in Table 81.

TABLE 81.—ANALYSES OF MALT EXTRACTS

	1	2	3	4	5	6	7
Extract lb. per 2 cwt.	70.4	71.0	70.1	69.9	69.7	68.0	70.6
Specific Gravity	1426.2	1430.0	1423.5	1421.6	1419.8	1415.0	1427.3
Diastatic activity Lintner	250.0	113.0	102.0	70.0	46.5	25.0	nil
Maltose per cent.	33.5	37.7	36.3	35.0	39.8	38.6	50.3
Glucose	21.7	15.7	11.0	19.5	13.8	7.1	2.6
Dextrin % (unfermentable)	6.7	8.8	13.8	14.5	10.5	15.6	21.6
Cane Sugar	2.5	1.6	3.0	3.6	2.9	3.2	2.6
Total Nitrogen	1.95	1.35	0.80	0.96	1.08	1.37	0.28
Permanently Soluble N	1.80	1.28	0.73	0.92	1.00	1.11	0.21
Ash	2.1	1.6	1.2	1.3	1.4	2.2	0.9
P ₂ O ₄	0.9	0.75	0.59	0.6	0.69	0.95	0.50
Water	19.7	19.6	19.9	19.4	22.5	23.0	19.3
Acidity as Lactic acid	1.06	0.92	0.54	0.86	0.77	0.75	0.22

Four distinct types are illustrated by these analyses.

(1) An extract with a very high diastatic activity, which only finds restricted use in brewing in circumstances in which its very high enzymic activity may be useful to supply a definite lack in the malts or to convert incompletely changed starch products.

(2) Extracts with diastatic activities about 100°-120° Lintner, which are most generally useful in the mash tun.

(3) Extracts at about 25°-50° Lintner, which may be used either in the mash tun or copper.

(4) Non-diastatic extracts used in the copper.

The diastatic types are suitable for use in the mash tun, where they are commonly employed at the rate of about 1 cwt. per 12 quarters of malt. It may be supposed that their enzymic activity is useful as a supplement to that of the malts. They undoubtedly usually contain proteolytic enzymes in an active condition and these may operate if the mashing temperature is not unduly high. In addition, their permanently soluble nitrogen, though small in quantity relatively to that derived from the malt, is probably useful for yeast nutrition, while, in conjunction with the inorganic phosphates, they provide buffering substances. The extent of this is roughly indicated by the results of titration to phenol-phthalein, expressed in the analyses as percentages of lactic acid.

It is difficult to draw definite conclusions from the analyses or interpret them in a way that can help in selection. The restrictions on the utility of diastatic activity determinations referred to in Section 177 apply with special force here. The enzymic activities appear to be high in comparison with ordinary malts and there can be no doubt that they are effective and include proteolytic and other activities in addition to amylolytic. Very little information is, however, available on these activities and it must not be inferred that they vary directly with the diastatic. Ordinary mashing temperatures also preclude any considerable exercise of their functions. It also does not necessarily follow that a malt extract with a high Lintner value is superior to another with a lower diastatic activity. It may have been made from a highly nitrogenous malt that originally had a much higher enzymic activity which was crippled to a certain extent in manufacture, with corresponding detriment in other ways.

The proportions of maltose, glucose and dextrin are also very uncertain criteria in the analysis. The apportionment of reducing and fermentable materials among these substances is entirely empirical and depends on calculations from the reducing and optical constants of three supposedly pure substances, while the extract may actually contain a very variable mixture of other starch conversion products. According to Ling⁷ the percentage of glucose, which he determined as glucosazone, may be considerably higher than that given in the above analyses. It varied between 17.2 and 22.0% in the samples examined. Ling was unable to detect the presence of maltase in the samples and suggested that glucose was formed by prolonged diastatic action during concentration in the vacuum pans.

Little information is available on the nature of the protein degradation products in malt extract, the formol-nitrogen is high and asparagine is present among other low molecular products. The quantity of such yeast-nutrient substances added to wort with the usual proportion of malt extract is small, but it may be significant, particularly when taken into account with the possible presence of Bios.

The colloidal composition of malt extract must also not be overlooked, some types, particularly those with low diastatic activity or non-diastatic, are added to the copper with results that show improvement in the foaming properties of the beer. How much of this is due to protein degradation products or to products of hemicellulose breakdown, which must exist in the extracts, is entirely unknown. The value of the extracts as malt adjuncts, whether on account of their enzymic activity, nitrogen content, buffering power, or colloidal properties, must consequently

be judged by trial and the most suitable type for any particular purpose selected on the basis of results.

UNMALTED GRAIN

(221) Malt Adjuncts.

The cost of malting and the loss of extract-yielding material during germination, amounting to between 7 and 12% of the dry weight of the original grain, has naturally led to the development of processes whereby they can be avoided or reduced by the use of unmalted cereals, rendered suitable for brewing by other methods of preparation. Together with the sugars, which can also be used as a source of extract, they are referred to as malt adjuncts, since they can only replace a proportion of the malt required in a brew. In Great Britain the law permits the use in brewing of malted or unmalted grain, other than barley, and of sugars, but this is not the case in all countries. There is no hygienic objection to prepared wheat, oats, maize, rice, unmalted barley or sugars as an alternative source of the starch or in partial replacement of the sugars existing in malt or produced from it in the mash tun. The arguments against their use are traditional or based on possible variation in the flavour of the product and on local agricultural conditions. The employment of malt adjuncts is limited in France to 15% of the total materials in order to encourage local agriculture and in Germany it is not permitted. The existence of large supplies of maize and rice in America and of rice in Japan has led to their use in greater relative proportions to the malt than in Europe. Their employment offers numerous technical advantages, quite apart from the question of cost, and these are particularly great in America on account of the type of barley grown.

(222) Raw and Prepared Grain.

Maize and rice provide by far the largest quantity of unmalted cereals employed in brewing. They are used in the form of grits, broken rice or flakes. The former are products of milling and, as they have not been cooked, they must be gelatinised in the brewery before their starch can be converted by the diastase of malt, with which they are mixed in the mash tun. This troublesome extra brewhouse process can be avoided by the use of flakes, in which the starch has been brought into such a condition that it is readily convertible in the mash tun. In both cases the manufacturing processes include removal of the bran, fibre and oil-bearing germs of the maize or aleurone layer of the rice.

Broken rice consists of the broken kernels produced in considerable quantity during the polishing of the grain.

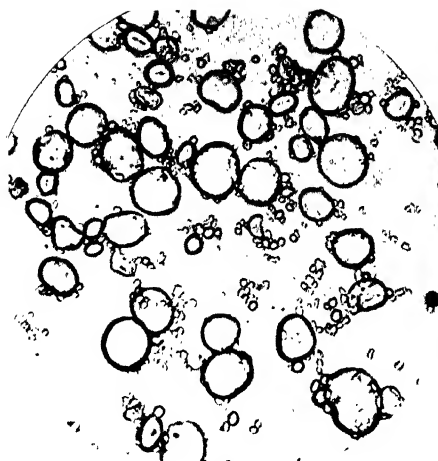
Barley, wheat, oats and rye are only used to a very limited extent, mainly in certain local beers, such as the Lambic of Brussels and the Peeterman of Louvain, for which 40 to 50 % of raw wheat is employed with barley malt, while oat flakes are used in some oatmeal stouts. The husks of oats are useful to supplement the drainage material in the mash tun, but they should first be steeped in water to remove flavouring substances and then dried before use. The starch of all the cereals can be converted by the diastase of malt after gelatinisation by boiling, so that any of them could be used as a source of extract. The chief objection to the employment of raw barley, wheat, oats and rye lies in the existence of protein and other nitrogenous substances which are soluble in water but apparently unacted upon by the proteolytic enzymes of malt. Thus barley mashed alone or with malt yields extracts containing the same quantity of nitrogen. The quantity of these substances in wheat and rye may amount to $2\frac{1}{2}$ or 3 % of the dry weight of the grain, but is insignificant in rice and maize grits, not more than $\frac{1}{4}$ or $\frac{1}{2}$ % respectively. The greater quantities give rise to instability and lack of brilliance.

The starch of all the cereals is probably ultimately of the same composition, but vary in physical properties and in the size and shape of the granules. Microscopical examination consequently provides the simplest method of determining the origin of flours, though considerable experience is required to distinguish some of the cereals with certainty, as their starch granules are very similar. The photomicrographs in Fig. 38 will help in distinguishing flours of barley, wheat, oats, maize and rice. The author is indebted to Mr. T. J. Ward for these photomicrographs and to the courtesy of Messrs. Eynon and Lane, for whose book on Starch they were prepared.

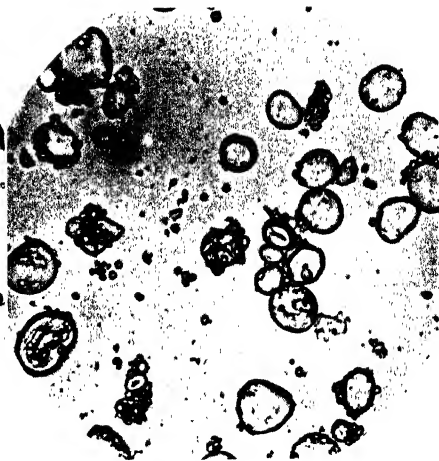
A typical protein is associated with most of the cereals, hordein with barley, edestin with wheat, zein with maize and oryzenin with rice. The protein composition of prepared rice and maize is, however, of little consequence since the insoluble proteins are not attacked or degraded to soluble products in the mash tun, even in flaked materials which have been submitted to a process that renders the starch very readily convertible by diastase.

(223) Composition of Cereals.

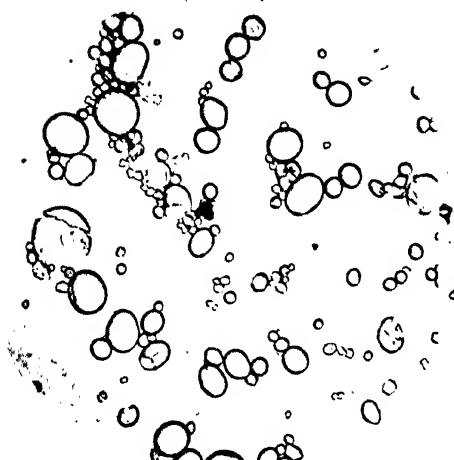
Approximate analyses^a of the most commonly used cereals are given in Table 82, reduced for comparison to a common moisture content of 10 %. "Crude fibre" represents the ash-free constituents of the grain after boiling for successive half-hour



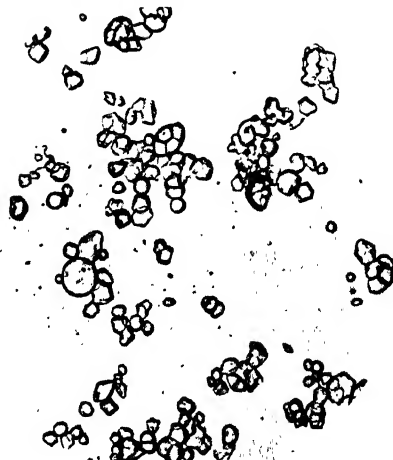
(1) Barley



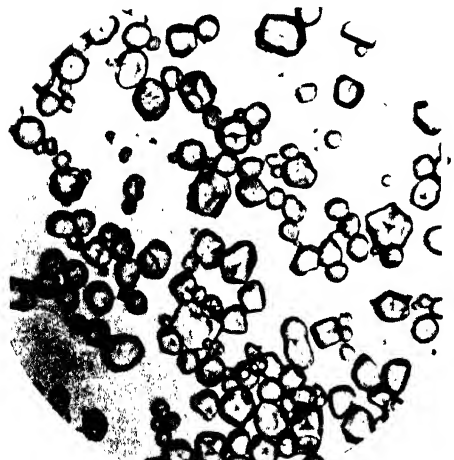
(2) Malt



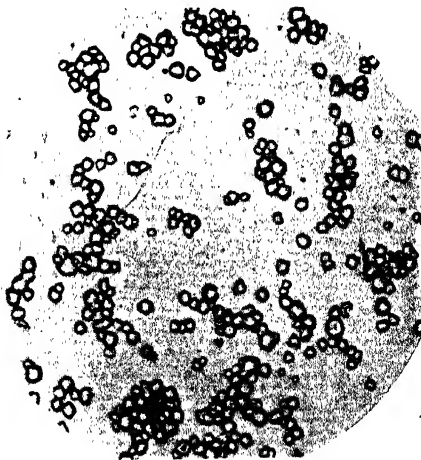
(3) Wheat



(4) Oats



(5) Maize



(6) Rice

FIG. 38
STARCH GRANULES ($\times 300$)

periods with $1\frac{1}{4}\%$ sulphuric acid and $1\frac{1}{4}\%$ caustic potash. It is consequently much lower than the percentage of husk, when present, or of the mash tun grains. The "soluble carbohydrates" are found by difference after determination of the other constituents. They are correspondingly higher than the percentage of carbohydrates capable of diastatic conversion in the mash tun. The latter may vary quite considerably in different samples of any of the cereal grains and may be 10 or 15% lower than the soluble carbohydrates of barley or oats, nearly as great as the latter in rice and 4 to 10% less in wheat and maize respectively. About 50% of the ash usually consists of P_2O_5 .

TABLE 82.—APPROXIMATE ANALYSES OF CEREAL GRAINS

	Barley	Wheat	Maize	Oats	Rice	Rye
Soluble carbohydrates ..	71.8	71.7	71.6	60.4	80.3	72.2
Crude fibre	4.8	2.0	2.2	10.7	1.5	2.1
Protein ($N \times 6.25$) ..	9.1	12.6	10.2	10.7	6.9	11.9
Ash	2.7	1.6	1.5	3.2	0.9	2.0
Oil	1.6	2.1	4.5	5.0	0.4	1.8
Water	10.0	10.0	10.0	10.0	10.0	10.0
	100.0	100.0	100.0	100.0	100.0	100.0

The carbohydrate and protein composition of the various cereals is not identical, but the differences are comparatively small. The comparatively large oil or fat content of maize is a disadvantage, but it is readily reduced to between 0.8 and 1.5% in the manufacture of grits by removal of the germ and aleurone layer, in the former of which fractions it exists in the greatest proportion, as is shown by the following percentages in the different parts of the grain.

TABLE 83.—COMPOSITION OF SEPARATED PARTS OF MAIZE
(PER CENT. ON DRY MATTER)

	Endosperm	Embryo	Hull
Carbohydrates, N-free extract ..	85.5	34.5	74.0
Crude fibre	0.5	3.0	16.5
Protein ($N \times 6.25$)	12.0	21.5	6.5
Fat or oil	1.5	30.0	1.5
Ash	0.5	11.0	1.5

The oil of most cereals has a characteristic flavour and odour. It also readily becomes rancid during milling or on exposure

to air and this becomes more marked as the oil content is greater. It is partly on account of its high oil content that maize is not used in the form of malt, malted maize retaining most of the oil and giving an unpleasant flavour to beer in which it is used. Small amounts of soluble substances which carry the odour or flavour characteristic of the oil may also occur with the latter. It is for these reasons and because the presence of oil in beer has detrimental effects on foam formation, that it is so necessary to reduce the oil content of the prepared products to as low a percentage as possible. The small quantity of oil remaining in flakes does not become rancid so readily as that of grits, since it is better protected from air during manufacture by the gelatinised starch. The oil of rice differs from that of maize in that it is almost tasteless and odourless, and does not become rancid on exposure to air. Little of the small quantity of oil in the prepared corn products is emulsified in mashing. The greater part remains in the grains with that from the malt, in which there may be 2 or 2.5%. Despite this, any flavour due to the oil may be communicated to the wort, emphasising the necessity for care in manufacture and purchase.

(224) Grits.

This is the name given to ungelatinised products prepared from the degermed kernel of maize or from rice. A number of grades are manufactured from maize, varying in the size of the fragments into which the separated endosperms are broken, and their freedom from oil, protein and other constituents of the germ, bran and aleurone layer. The corn is first freed from impurities by screening and washing in a counter-current of water. After which it is conditioned in low-pressure steam, which softens the germ, skins and outer layers of the endosperm and brings the moisture content up to that necessary to facilitate the subsequent processes, in which it is subjected to friction in decorticators, where the germ, bran and aleurone layer are separated from the endosperm, and the degerminated corn screened. The fraction delivered through the screens is "through stock" and the other portion is pearl hominy with some bran and flour but practically no germs. The through stock containing pearl hominy and smaller grits, with meal, germs, bran and feed in all states of division, is subjected to further screening until mixtures of white material and germs are separated. These are delivered to corrugated rolls, which crack the grits but flatten out the tough and rubbery germs, which are separated on bolters. The grits or hominy are reduced to proper size and classified

by passage through break rolls which vary in size of corrugations and clearance and in which the grits are subjected to a sheering action, as one pair of rolls turns at a higher speed than the other. This results in the production of a series of products varying in size and known respectively as coarse or brewers' grits, fine grits, degerminated meal, corn meal and flour.

The germs which have been removed are ground between steel rolls, after which the product is steamed in a jacketed vessel and pressed hot in hydraulic presses at about 3 tons per square inch to separate the oil from the cake. The former is used in the manufacture of soap and glycerine or refined for table and pharmaceutical purposes. The cake is used in cattle feeds.

Since rice has no oil-bearing germ, the manufacture of rice grits differs slightly from that of maize grits. The oil of the kernel is contained in an inner skin or aleurone layer, which must be rubbed off during milling and removed as well as the bran by the process of polishing.

(225) Refined Grits.

The so-called "refined grits" are almost pure maize starch, prepared from yellow corn by the wet nulling process in which, after steeping, the starch and gluten are separated from the germ and fibre by processes of milling and sedimentation in water. The steeping extracts soluble matter and softens the corn sufficiently to facilitate the separation of undamaged germs when it is broken in attrition mills. Subsequent treatment with running water in rectangular separating tanks carries the germs over a weir. The heavier sedimented material is mixed with water, ground in Buhr mills of stone and passed over shaking tables covered with fine mesh silk, through which the starch and gluten pass. These are separated by passage over long, slightly inclined troughs or starch tables, on which the starch deposits in a cake, which is finally washed in continuous rotary washers, giving a practically pure cake of starch, ready for drying. Starch prepared in this manner is also used for making corn syrups.

(226) Flakes.

In order to avoid the extra process of cooking or boiling in the brewery, grits are gelatinised and rolled into thin "flakes" of a quarter- or half-inch diameter, readily converted when mixed with malt in the mash tun. In the process of manufacture, grits of suitable size are slowly cooked to gelatinise the starch, with precautions to avoid vitrification by over-rapid heating. The product is partly dried and then passed through heated

rolls under sufficient pressure to yield the flakes in as thin a state as possible but unbroken. The flakes are finally submitted to a current of dry air in a special drying machine until they are crisp but not so dry that they crumble in packing. They usually contain about 8% of moisture when weighed in the factory and dispatched. The moisture content may increase to 10 or 12% during transit to the brewery, or during short storage before use, so that the original weight of the sacks should be accepted in the brew house, or the moisture determined in order to ascertain the extract available from weighed quantities. Storage with excess of moisture may lead to the development of mould and a musty flavour.

Rice flakes are white, maize flakes may be bright golden yellow or white according to the maize from which they were made. Oat flakes are a duller white than rice or maize flakes and of softer texture. The flakes should be uniform in size and free from broken fragments or dust. Vitriified flakes and unflaked material should be absent and there should be no oily or musty odour. The thinner the flakes the more rapid and complete will be their conversion in the mash tun, provided they are intimately mixed with the malt, to effect which a special feeding and mixing device may be attached to the grist case or malt elevator.

(227) Composition of Grits and Flakes.

Average approximate analyses of grits and flakes are given in Table 84. The starch represents the percentage of carbo-

TABLE 84.—APPROXIMATE COMPOSITION OF GRITS AND FLAKES

	Maize grits	Refined grits	Broken rice	Flakes		
				Maize	Rice	Oats
Starch, etc.	82.7	91.5	83.6	80.0	81.5	66.0
Protein (N \times 6.25) ..	7.5	0.2	7.0	8.0	7.5	14.0
Oil and fat	1.0	0.05	0.6	1.0	0.4	8.4
Ash	0.3	0.15	0.3	0.3	0.5	0.6
Cellulose, fibre, etc. ..	0.5	0.1	0.5	2.7	2.1	3.0
Moisture	8.0	8.0	8.0	8.0	8.0	8.0
	100.0	100.0	100.0	100.0	100.0	100.0

hydrate matter which is convertible to soluble extract in the mash tun and is considerably higher than in barley malt. Consequently maize and rice grits and flakes yield a higher extract than malt, even when they are used with a moisture content

6 to 10% greater than that of the malt. The protein content is very similar to that in malt, but the insoluble proteins are not degraded by the proteolytic enzymes of malt and yield very little, if any, soluble nitrogen to the wort. The oil or fat percentage in maize should not be greater than 1.5 but may be as low as 0.7% and does not generally exceed 1.3% in well-made flakes. It is determined by extraction with light petroleum spirit and not by ether, which dissolves substances other than fat or oil. A comparatively high percentage is frequently found in samples containing broken flakes or debris. Rice products contain a much lower percentage of oil than maize flakes or grits. About 50% of the ash consists of P_2O_5 .

Although grits and flakes contain no husk, they do contain a moderate percentage of cellulose and fibre, derived from the structural elements of the endosperm. Owing to this, the flakes do not impede mash tun drainage if they were originally thoroughly mixed with the malt. Grits, when properly gelatinised, also do not materially decrease the speed of running off worts from the mash tun but, if imperfectly gelatinised, they may set to a jelly and clog the grains or even set in the pump or main delivering the cooker mash to the mash tun.

No such analysis as those given in Table 84 is necessary in judging the brewing value of maize or rice products. It is usually quite sufficient to determine the extract, moisture and oil, though the nitrogen content is also occasionally estimated. The extract may be determined in the wort obtained by mashing a known proportion of the grits or flakes with malt and correcting the specific gravity by that given by the malt alone. Flakes are mixed directly with the malt, but grits must previously be gelatinised by boiling with water. This method has the disadvantage that different malts give a different extract from the same sample of flakes or grits. Better results are obtained by using a cold water extract prepared from malt with a diastatic activity between 30° and 40° Lintner, according to the standard method of the Institute of Brewing.⁹ A solution of a highly diastatic malt extract syrup may also be used with success for the conversion, but it is generally necessary to use it at such a dilution as will give a control having a specific gravity between 1010 and 1020. The moisture content must be taken into account when judging the extract. The sum of the extract in Brewers' pounds per quarter of 336 lb. and the moisture should be above 110 in the case of maize flakes. High-class maize flakes frequently give 115 and flaked rice about 120. The moisture content should not be higher than about 12%. The nitrogen content is determined by the Kjeldahl process and from it the

protein content is assessed by use of the factor 6.25. High figures involve a reduction in extract. Comparative extract yields on dry substance are given in Table 85.

TABLE 85.—EXTRACT OF GRITS AND FLAKES ON DRY MATTER BASIS

	Brewers' pounds per 336 lb. dry material
Maize grits	105-115
Refined grits	120-130
Broken rice	105-115
Maize flakes	105-115
Rice flakes	110-120
Oat flakes	85-95

The moisture content of flakes should not exceed 10 to 12% when used, not that a higher percentage would mean a lower extract in the mash if the flakes were weighed at the factory with an approximately constant moisture content, the sacks when used being considered to contain the stated weight and not the increased weight due to the absorbed moisture. A possible effect of increased moisture content is, however, a reduced initial heat from the same striking heat, owing to the smaller rise of temperature produced when moist material is mixed with water, in comparison with that obtained with the same material in a dry state. A higher moisture content may lead to rapid deterioration in storage and possibly to the development of mould and a musty flavour.

(228) Use of Grits and Flakes.

The flavour and other properties associated with beer demand malted barley as the main extract-giving material. Its diastase is also essential for the conversion of any grits or flakes which may be used with it, but these must alter the character of the beer to some extent as they lack the aromatic properties of malt. Rice in particular produces a drier, less fully flavoured beer which may be appreciated in some countries but must be counter-balanced in others by a proportion of highly flavoured malt. This is generally possible without unduly raising the colour of the beer and the production in this way of a pale beer with full flavour constitutes one of the advantages of grits and flakes in suitable blends with malt. Other advantages are found in the production of very pale beers, in the high extract yield of rice and maize and in the reduction of wort nitrogen, when they are used with malts of comparatively high nitrogen content. They

also yield very little if any buffering substances to the wort. This permits of a readier increase of acidity during fermentation, with corresponding increase in the stability of the beer. These technical advantages are usually accompanied by a considerable economy in cost, due to their lower price and higher extract. Oat flakes are in a rather different category, and their use in oatmeal stout is suggested rather by considerations of flavour and nutritional value.

The extract of the grist is almost always increased and the wort may be enriched with readily fermentable carbohydrates when grits or flakes are used, providing the conversion has been satisfactory. In most infusion mashes, however, the replacement of about 4% of malt by maize flakes leads to an increase of 1° in the $[\alpha]_D$ of the wort, at the same mashing temperature. The use of grits or flakes affords a more definite means of controlling the carbohydrate composition of wort or its limiting attenuation than is available through change of temperature in a malt mash. The grits are first gelatinised by boiling, the temperature being slowly raised to the boiling point in presence of a proportion of malt, which facilitates the subsequent gelatinisation by a restricted diastatic attack on the starch with very little conversion. The gelatinised grits are then pumped over to the malt mash, and the temperature at mixing can be readily controlled to give a highly fermentable or dextrinous wort. If, however, the mash temperature is too high or the malt is deficient in converting power, insufficiently degraded products result. These tend to change slowly later, with deleterious effects on fermentation and stability. Since the gelatinised starch must be liquefied before it is saccharified, it is essential that the liquefying activity of the malt should be adequate, which is not always the case as the activity of the liquefying and saccharifying functions of diastase do not necessarily run parallel. To avoid this occasional lack of liquefying activity in malt, it has been proposed to make use of diastatic preparations from bacteria, which have a very high liquefying activity with comparatively low saccharifying power.

Reduction in nitrogen content is the most important alteration in wort composition produced by substitution of grits or flakes for a proportion of the malt.¹⁰ This is due to the inability of the proteolytic enzymes of malt to degrade their proteins, and its extent can readily be calculated, since it is proportional to the percentage of adjuncts used. Whether this reduction in wort nitrogen is of advantage or otherwise depends on the nitrogen content of the malt, the gravity of the wort and the type of beer required, all of which must be carefully considered when deciding on the grist. A certain percentage of protein degradation

products is essential in wort for yeast nutrition, fulness, head retention, etc., while excess may lead to defects in brilliance and stability. Maize and rice are to be considered as nitrogen diluents and in no case should they be used in such quantity as unduly to reduce the useful properties associated with the nitrogen of malt. On the other hand, they are particularly valuable for reducing the nitrogen content and thereby increasing the stability of beer subject to early formation of haze, particularly after pasteurisation. For example, it may be found desirable to reduce the nitrogen content of beers of 1048–1052 original gravity from 0·6 or 0·7 mgm. per 100 ml. to 0·5 mgm. in order to ensure adequate stability.

Fermentations are liable to suffer if more than a very small proportion of rice or maize is used with low nitrogen malts, unless the gravity of the worts is fairly high. 10 to 20% may generally be used with well-made malts containing 1·5 to 1·6% of nitrogen and having a diastatic activity around 30°–35° Lintner, while 25 to 40% and sometimes even more is commonly employed in American lager beers with Manchuria malts having a nitrogen content of 2% and a diastatic activity of about 100° Lintner.

(229) Summary.

Certain special types of malt and unmalted cereals are used with ordinary malts, which constitute the major part of the extract-yielding materials of brewing. The former include roasted malts which are used in small percentage to give colour and flavour, particularly with stouts. The black malts are roasted in revolving cylinders after kilning, while crystal malt is made in a similar manner from green malt. The colour and flavour characteristic of amber and brown malts may be obtained on the kiln or by roasting in cylinders. In addition, there are a few types of malt in which such properties as acidity or colour, in conjunction with moderate diastatic activity, are emphasised by special malting methods; among these are the proprietary Enzymic and Diamber malts. Small quantities of wheat and oat malts are also used in some beers, the former adds fulness and foaming capacity but may, if under-modified, give a tendency to turbidity in beer. Oat malt is used, mainly in oat malt stouts, for its flavour and nutritive properties.

Unmalted cereals, maize and rice being the most important, are used as a source of starch and extract with ordinary malts supplying the converting enzymes. They are used either in the form of grits or flakes, the former being a product of milling which must be gelatinised by boiling in the brewery before its

starch can be converted by malt diastase. The process of manufacture removes husk, bran and the oil-bearing parts of the maize or rice. Rice is often used in the form of the broken kernels produced in milling and polishing. Flakes are produced from maize grits, rice and, to a smaller extent, oats, by cooking, rolling and drying. This so alters the starch that it is directly and readily converted by malt diastase when intimately mixed with the grist at mashing. The proteins of maize and rice grits or flakes are about equal in quantity to those of malt, but they are not degraded by the proteolytic enzymes of malt. These materials consequently supply no nitrogen to the wort and may be regarded as nitrogen diluents, for which reason they are valuable for increasing the stability of beers brewed from high nitrogen malts, or in cases where the nitrogenous substances present are liable to produce an early haze. On the other hand they may, if used with low nitrogen malts, unduly reduce the quantity of yeast nutrients in wort. They are also useful in the production of very pale beers and are economical sources of extract. An important result of their use is reduction in the buffer content of worts.

Malt extract is a syrup produced by concentrating in vacuum pans the wort produced from very lightly cured malts by mashing at low temperatures. They therefore retain the diastatic and other enzymic activities of the original malts. In addition they contain the low molecular protein degradation products formed by mashing between 120° and 130° Fahr. and hence provide yeast nutrients and buffer substances which regularise the reaction of the mash and tend to counteract any abnormalities which might otherwise occur.

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SUGARS

SPECIFIC GRAVITY, EXTRACT AND POLARIMETRY

CHAPTER XIV

BREWING SUGARS

(230) Sugars as Malt Adjuncts.

Various sugars and starch conversion products can be added in the copper to supplement the fermentable extract formed in the mash tun by conversion of the starch of malt, but similar restrictions in respect of the quantity used apply as with cereal adjuncts, on account of the lack of nitrogenous yeast nutrients. They provide a means for varying the composition of wort, within limits set by the requisite balance between sugars and non-sugars, supply extract which may be either entirely or only partly fermentable, give characteristics of fulness and flavour that are appreciated in some cases, increase the stability of beer by replacement of nitrogenous extract and yield beer that will become more readily and rapidly brilliant than when brewed with malt alone. Primings are strong solutions which must not, in this country, exceed 1150 specific gravity but should not be much less. They are sometimes added in the fermenting vessel at the close of primary fermentation but, more frequently, in storage tank or cask to promote rapid condition and, in some cases, on account of their flavour. The sweet and luscious flavour of some sugars does not entirely disappear when the sugar has been fermented, but gives additional fulness to the beer. In some cases, sugars which are not entirely fermentable are selected.

The sugars used in brewing comprise

- (1) Cane sugar, derived from the sugar cane and, much less frequently, from sugar beet.
- (2) Invert sugar, made by inversion of cane sugar.
- (3) Starch sugars, including corn syrups and glucose, manufactured by conversion of the starch of cereals, usually maize.
- (4) Mixtures of these, their utility in copper or cask depending on their flavour and fermentability.
- (5) Caramels, made from cane sugar or glucose.
- (6) Lactose or milk sugar, which is only used in very small quantity in some milk stouts.
- (7) Honey, even less used.

Maltose, which might appear to be the most suitable sugar to replace that formed from malt in the mash tun, is not used in the

pure state, but exists as a constituent of corn syrups with dextrin and glucose. Lactose differs from cane sugar, invert sugar, maltose and glucose in that it is unfermentable by ordinary brewery yeasts, while certain of the higher starch conversion products are appreciated because they are only partly or slowly fermentable.

(231) Cane Sugar.

The sugars obtained from the sugar cane, sugar beet, sugar maple, certain palms or the stem of sorghum are, when purified, of identical chemical composition. All of them are sucrose. The natural juices from which they are derived, however, differ very considerably in flavour owing to the many other substances which they contain. For example, the root of the beet contains a larger proportion of mineral salts than the sugar cane and decomposition products are formed with the larger quantities of lime necessarily used in the course of clarification, which give an objectionable flavour to the juices and raw sugar. These render the latter unfit for consumption until refined. The raw sugars from the cane are, on the other hand, very luscious but they do not all taste the same, varying considerably according to the place in which the cane was grown or the treatment they received during extraction and preparation, characteristic differences being found in sugars from Cuba, Java, Barbadoes, Trinidad, St. Domingo, Mauritius, etc. Since the value of cane sugars in brewing depends so largely on the flavours they communicate, even after all the sugar itself has been fermented, the principal source must be the sugar cane, which yields juices possessing these properties in their most attractive form. The final product of the refineries, from whatever source it originally came, is among the purest substances commercially obtainable, but it lacks the distinctive characteristics of flavour demanded in brewing. As a source of carbohydrate extract it is unexcelled and can be used without hesitation under circumstances in which those flavours are not required, but the raw or partially refined sugars from the cane are more attractive in most cases.

The raw sugars are prepared by processes which include shredding of the cane and maceration of the milled fibres, until about 97% of their sugar content is obtained in a water solution or juice. This is defecated with lime, frequently with the addition of a small quantity of phosphate, the reaction being adjusted very closely to neutrality, and filtered to remove precipitated protein and other organic impurities. The clarified juice is concentrated by multiple evaporators until crystallisation

sets in and *massecuite* containing 93% of solids is obtained. After treatment in crystallisers the *massecuite* is passed to centrifugal machines which separate the molasses from the sugar crystals. The purity of the sugar so obtained is determined by polarisation and is usually 96 to 99% pure sucrose. Second and third crops of sugar polarising between 86 and 93% or as low as from 78 to 80% may also be secured from the molasses. Usually the lusciousness of the sugars increases with greater proportions of other substances derived from the cane, some of which are in a colloidal state, and many such sugars, among them West Indian and Brazil sugars of comparatively low polarisation, are used in brewing on account of the fulness and sweetness they give. Other low polarising sugars, such as that from Mauritius, have a somewhat acrid after-flavour. On account of these different flavours, great care must be exercised in selecting brewing sugars, fermentation tests being desirable as the original flavour is not always a good guide to that left after the sugar itself is removed.

The sugar is extracted from beet by water in batteries of diffusion cells and afterwards purified in a manner somewhat similar to that adopted with raw sugar from the cane, but it is necessary to obtain a considerably purer product from the beet, in the form of white crystals polarising almost 100%, before the salts and objectionable flavours are eliminated. The crystals are indistinguishable chemically from similar crystals obtained from the cane, and can be used in place of the latter without detriment when pure. Occasionally the crystals polarise slightly over 100% on account of the presence of traces of raffinose.

Cane sugar is used both in the copper and as a priming. Raw sugars of good class are generally employed for the former purpose and when of suitable purity should not contain excess of undesirable substances or micro-organisms. Sugars of this type and pure crystals can also be used for priming, but candy sugar is preferred by many. Cane sugar is rapidly inverted when added to cask, the change being generally complete in about 24 hours. This process is believed to be an essential preliminary to fermentation. It is carried out by the enzyme invertase or sucrose secreted by the yeast and does not appear to affect the fermentative activity of the yeast or influence the rate of fermentation. Baker and Hulton¹ found that cane sugar and invert primings were fermented at substantially the same rate in beer under ordinary cellar conditions and that about one-third of either sugar still remained unfermented after 7 days in cask when added at normal priming rates. The following are analyses of cane sugars used in breweries.

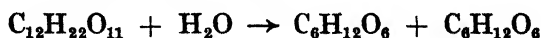
TABLE 86.—ANALYSES OF CANE SUGARS

	Refined crystals	Candy sugar	Brown sugar	Brown sugar	Yellow crystals
Polarisation % cane ..	99.97	99.6	85.0	90.0	96.0
Reducing sugar, as invert ..	—	—	3.0	2.0	1.3
Ash	0.01	0.1	3.0	2.0	0.6
Water	0.02	—	4.4	3.0	1.0
Other organic matter ..	—	—	4.6	3.0	1.1

The yellow crystals represent the high grade products turned out at many cane factories, and of which Demerara sugar is well known. Beet crystals are sometimes dyed to imitate these. This can be detected by making a solution alkaline and shaking with ether which extracts yellow colouring matter with a greenish fluorescence. The meaning of polarisation is given in Section 244. It is always less than the actual percentage of cane sugar, since the reducing sugars are lævo-rotatory. The brown sugar polarising 90 should be a good grade for brewing, with fine flavour, while the lower grade at 85 should have a very luscious flavour and be useful also for making invert sugar.

(232) Invert Sugar.

The chemical nature and characteristic properties of invert sugar are described in Sections 108 and 109, where it is shown to be a mixture of equal quantities of glucose and fructose produced by hydrolysis of cane sugar. This process is known as inversion and the product as invert sugar, because the positive angle shown by a solution of cane sugar in a polarimeter is changed to a negative angle at the close of the reaction. The latter consists essentially in the breakdown of the molecule of cane sugar, with the addition of the elements of a molecule of water, so that 342 parts by weight of cane sugar become 360 parts of invert sugar. Invert sugars are usually manufactured from selected raw cane sugars and occasionally from refined crystals, the hydrolysis or inversion being effected by means of dilute acids, generally sulphuric or less frequently hydrochloric, or occasionally by yeast, the reaction in either case being



The cane sugar is dissolved in water, in iron vessels fitted with steam coils, and brought to a specific gravity of 1250–1800 at 180° Fahr. The necessary amount of acid, which may be 0.65% of 78% sulphuric acid if the raw cane sugar polarised 96° or 1.0–1.5% if it was of lower class, is diluted with water and added to

the sugar solution, the temperature of which is raised to 200° Fahr. The progress of inversion is followed polarimetrically and marked by the gradual fall of the positive rotation of cane sugar until the negative reading due to invert sugar is obtained. The final angle is never that of pure invert sugar, given in Table 94, but as soon as a satisfactory approach to this is noted, the acid is neutralised with powdered chalk or sodium carbonate, according as sulphuric or hydrochloric acid were used for inversion, and the p_H adjusted to between 6.5 and 7. Some of the fructose would be destroyed if the reaction with acid were carried too far and the angle would again rise, since the negative rotation of invert sugar is due to that of fructose, glucose having a smaller positive angle. In consequence the inversion is rarely quite complete and a small percentage of cane sugar almost invariably remains unchanged. The inverted sugar is filtered through presses to remove precipitated calcium sulphate and other impurities. The bright filtrate is then passed through towers containing active charcoal to remove some of the colour and impurities which would be detrimental to its brewing value. This purification must not be too drastic, otherwise desirable substances which contribute to the flavour and fulness of beer would be removed by adsorption on the char. Finally the syrup is concentrated in vacuum pans until it weighs 14 to 14.2 lb. per gallon and run to trade containers. When refined sugar crystals are used for inversion, the quantity of acid can be reduced to about 500 ml per ton of sugar so that subsequent neutralisation is scarcely necessary.

Inversion by yeast is only infrequently adopted by invert sugar manufacturers but is sometimes employed by brewers as a simple process in which difficulties attending acid hydrolysis, neutralisation and filtration are avoided, though the flavour of the product is not so luscious as that of acid-inverted sugar. The resulting, possibly incompletely inverted sugar, can be added to the copper with its accompanying yeast. A solution is made containing 80–40% of raw cane sugar and the temperature is raised by live steam to 133° Fahr. at which the activity of the secreted enzyme, invertase, is great but at which fermentation is prevented. Yeast is then added at the rate of $2\frac{1}{2}$ to 3% of the sugar used and the temperature maintained until inversion is sufficiently complete as shown by approach of the $[\alpha]_D$ of a sample to that of invert sugar, 19.6°. Purer sugars may be inverted by this method in 4 or 5 hours, but a much longer time is required with sugars polarising about 85°. After inversion the yeast may be killed by raising the temperature to 200° Fahr. and the sugar purified as in the acid process if desired, though neutralisation is obviously unnecessary.

Three grades of invert sugar are commonly made in England, Nos. 1, 2 and 3, differing in degree of purification. The sugar is sold either in the syrup or solid form in casks, pails and cartons or bags of paper or card. The syrups tend to solidify in the casks or pails on account of crystallisation of the glucose, so that special dissolving plant with a steam jet projecting through the bung-hole of the cask is required, as is described elsewhere. The extract is usually guaranteed at 72 lb. per 224 lb. and may be rather higher, as in the typical analyses in Table 87. The quantity of un-inverted cane sugar should not be much higher than that given. The percentage of protein and ash is usually very small and the iron content should not exceed 0.005%. Quantities exceeding 0.1% are liable to cause discoloration of the beer and excess may sometimes be detected by blackening of the hops in the copper with tannate of iron.

Invert sugars are very suitable either for copper use or as primings. They are characterised by ready fermentability and by their pleasant luscious flavour. The No. 1 or No. 2 sugars are used for pale ales and No. 2 or No. 3 for mild ales.

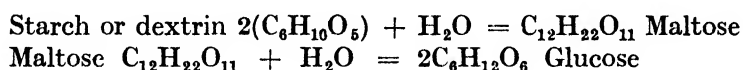
TABLE 87.—ANALYSES OF INVERT SUGARS

	No. 1	No. 2	No. 3
Extract, Brewers' lb. per 224 lb. ..	73.2	73.0	72.5
Colour	30	50	120
Specific rotary power $[\alpha]_D$	—14.2	—13.9	—12.0
Invert sugar %	78.9	76.9	76.2
Cane sugar %	1.3	1.5	2.0
Protein ($N \times 6.25$) %	0.3	0.3	0.5
Ash %	0.3	0.5	0.6
Iron %	0.001	0.002	0.003
Water %	15.7	16.2	16.7
Undetermined by difference	3.5	4.6	4.0
	100.0	100.0	100.0

The proportion of fructose in invert sugar is always rather less than that of the glucose, generally 1 to 1.5% less. The undetermined matter contains a certain amount of unfermentable reducing substances, for which a correction should be made in calculating the percentage of invert sugar by means of its reducing power. The protein should not much exceed the percentages given in the Table but the ash may occasionally reach 1.5–2.5%. It is difficult to detect the use of high grade raw beet sugars in invert, though the nitrogen content may be somewhat increased.

(233) Starch Sugars.

These sugars are manufactured by the hydrolytic action of dilute acids on starch, usually maize but sometimes sago, tapioca and potato starch are used as the raw material. The starch is made into a cream with water, the necessary small amount, about 1%, of sulphuric or hydrochloric acid, usually the latter, is added and the mixture transferred to a converter in which it is heated by direct steam until a pressure of 60 to 80 lb. per square inch is attained. The reaction consists in breakdown of the molecule of starch by hydrolysis into dextrins, and then successively, maltose and glucose. The chemical nature of these reactions, reduced to their simplest terms, may be represented by



The change from starch to glucose can be followed polarimetrically, a fall of angle being noted as the percentages of dextrin and maltose successively fall and that of glucose rises until it is the only sugar present, but it is not referred to as inversion, since the angle never becomes negative. The optical activities of soluble starch and dextrin are generally taken as 202° and 195° respectively, those for maltose and glucose are given in Table 94. Although the first product of starch conversion is referred to as dextrin and a percentage of the latter is given in analyses as if it was an individual entity, there are probably a number of intermediate products between starch and maltose and the term dextrin can only be taken as a convenient designation of the unfermentable substances or to represent a percentage of the product, calculated from the analytical figures on the assumption that it has an $[\alpha]_D$ of 195° , for example, and no reducing power. Coincident with the fall of angle there is an increase in reducing power, as the molecule is reduced in size to that of maltose and ultimately glucose.

The acid used is not represented in the equations for the reactions, since it acts only as a catalytic agent in the hydrolysis and remains at the close of conversion. When this has been carried to the extent required to produce pure glucose or the mixture desired, the acid is neutralised by chalk or sodium carbonate, according as sulphuric or hydrochloric acid were used. The product is purified by addition of sulphurous acid and by means of centrifuges or filter presses and sometimes char filters. In these purification processes most of the calcium sulphate or salt produced on neutralisation, with colouring matters, nitrogenous substances, oil and any traces of fibre are removed. Careful

neutralisation is important, as slight alkalinity tends to promote caramelisation. Hence a p_H value of 5 is aimed at. The solution is finally concentrated to a syrup or sufficiently far to crystallise when seeded. The following are typical analyses of solid glucose, which is a very useful brewing sugar for drier flavoured beers.

TABLE 88.—ANALYSES OF GLUCOSE

	1	2
Water	13.7	16.2
Glucose	70.0	67.0
Maltose	2.8	3.3
Protein	0.4	0.3
Ash	0.5	0.9
Unfermentable matter	12.6	12.3
	100.0	100.0
Extract lb. per 224 lb.	75.0	73.2
[α] _D	50.0	46.0
Iron %	0.003	0.005
Colour	60	80

Glucose crystallises with one molecule of water as $C_6H_{12}O_6 \cdot H_2O$, in which form it contains 9.1% of water and should give an extract of nearly 78 lb. per 224 lb. With 10% of water it gives up to 77 lb. and with 15% of water about 73 lb. It is readily fermented in moderately dilute solutions in presence of the necessary nitrogenous and mineral yeast nutrients, but commercial glucose leaves an unfermentable residue, containing a product of decomposition formed by the action of the dilute acid and to which the name of gallisin is usually applied.

Incompletely hydrolysed syrups, containing varying percentages of maltose and dextrin and known as corn syrups, glucose syrups or dextrin-maltose are also used in brewing. They are very different in flavouring properties from invert sugar or raw cane sugars, being almost neutral in that respect. They are consequently more suitable for use in the drier types of beer, particularly lager beers. If the conversion is stopped as soon as all starch has disappeared, as shown by the iodine test, the product is only slowly and partially fermentable. Sugars of this type are known as dextrin-maltose. As conversion proceeds a greater proportion of the fermentable sugars is produced, so that various grades suitable for slowly fermenting primings

are obtained and are useful for giving slow condition in casks without undue sweetness. Analyses of three types are given in Table 89.

TABLE 89.—ANALYSES OF CORN SYRUPS

	Low Fermentable	Medium Fermentable	High Fermentable
Extract, Brewers' lb. per 224 lb. ..	73.0	73.0	73.0
Specific rotatory power $[\alpha]_D$	145.0°	135.0°	120.0°
Colour	40	40	40
Iron, per cent.	0.005	0.005	0.005
Readily fermentable solids %	40	50	60
Glucose	12.0	19.0	28.0
Maltose	37.0	39.0	37.0
Unfermentable	33.0	24.0	17.0
Proteins	0.5	0.5	0.5
Ash	0.5	0.5	0.5
Water	17.0	17.0	17.0

(234) Priming and Copper Sugars.

A large number of proprietary brands of mixed sugars, with characteristic differences in their fermentability, flavours and other properties are available. These usually consist of glucose, corn syrups, cane sugar and invert sugar in various proportions, to which caramel may be added or the desired flavour and colour given by partial caramelisation. Many of them are intended to be used as sources of partly or difficultly fermentable extract, particularly when lusciousness combined with the unfermentability of dextrinous syrups is required. They are used in the copper for mild ales and stouts, and as primings. The extracts of these sugars vary from about 65 to 75, their colours from quite pale syrups to black caramel mixtures with a colour of 8,000 or more. Their optical activities are very varied, according to the nature of the constituent sugars and may be as high as $[\alpha]_D$ 110° or down to 20° with a mixture of invert and cane sugars and a negative angle with black invert sugars. A satisfactory analysis is an extremely difficult matter and must depend on very arbitrary assumptions in regard to the fermentability of the constituents. The readily fermentable matter may vary from 80 to over 70% and the difficultly or unfermentable from about 10 to 50%.

The composition of some typical mixtures is given in Table 90. The invert sugar in (a) may be No. 1 or of lower grade, according as the sugar is intended for pale ale or mild ales, or it might be replaced by raw cane sugar for fuller flavoured beers. (b) is not as sweet and is suitable for pale or bitter beers. A mixture

containing 20% of malt extract with 40% each of invert sugar and glucose may prove useful with poorer malts. (c) and (d) are suitable for stouts in the copper or as primings, respectively.

TABLE 90.—COMPOSITION OF MIXED SUGARS

Sugars	Readily fermentable %	Unfermentable %	Extract lb.	[α] _D
(a) Glucose 50% Invert 50%	55	28	72	66°
(b) Glucose 70% Sugar candy 30%	39	42	72	90°
(c) Raw Cane, partly inverted	Invert 23% Cane 47%	10	68	28°
(d) No. 4 Invert 90% Refined Molasses 10%	69	12	72	-2.7°

(235) Caramel.

Caramel is the name given to the soluble, dark-coloured product obtained from sugars by the action of heat alone or by the joint action of heat, acids, alkalis, ammonium salts, etc. When cane sugar is carefully heated it melts about 160° C. and gives a clear, pale yellow liquid, from which only part of the sugar can be regained in a crystalline form. If the heat is maintained, the composition of the sugar changes and above 180° C. it becomes brown and loses weight. Frothing occurs at temperatures between 210° and 220° C. and the liquid darkens continually, giving off water with traces of volatile organic substances and is finally converted to caramel, with some insoluble carbonaceous matter if the temperature becomes too high. The nature of the products is very doubtful, but three fractions, differentiated by varying solubility, have been separated and referred to as caramelan, caramelen and caramelin, of which the two first are crystalloid and the third colloidal.

Glucose heated alone does not produce a satisfactory caramel, but does so when small proportions of organic acids, caustic alkalis, ammonia, ammonium or alkali salts are added. The products differ in flavour and other properties, and the best methods of manufacture have been worked out by trial to produce caramels of high tinctorial value, lacking in acidity and insoluble matter. Apparently the caramels produced from cane sugar and glucose are very similar and most of those used for colouring beer are produced from the latter sugar. McCowan's process was developed into one of the earlier successful manufacturing

methods. According to this, glucose is heated for 24 hours at 212° Fahr. with from 5 to 10% of its weight of liquor ammonia in a closed digester. An alternative process described by A. G. Salamon and E. N. Goldie,² consists in melting 5 cwt. of glucose and adding 45 ozs. of ammonium carbonate and 15 ozs. of ammonium chloride when the liquid has been brought to the boil at 230° Fahr. The mixture is boiled until it swells up to about double the original volume and greyish-green vapours are evolved. This occurs at about 310° Fahr. and takes a considerable time. The caramel produced can be solidified by pouring on to iron plates or reduced to a syrup of the desired density by addition of water.

The ammonia processes are much more certain and under better control than those depending on the direct action of heat, but the product necessarily contains a considerable percentage of nitrogen, varying between 0.3 and 5%. It is not known in what form this nitrogen exists in combination with the sugar, but condensation products of the melanoidin type may occur. The nitrogenous substances do not appear to be assimilable by yeast or to reduce the stability of beer to which normal quantities have been added. (Briant.³)

Caramels are used primarily for colouring, but their flavouring properties are of considerable importance. The flavour of the sugar changes during manufacture, developing at first a characteristic lusciousness which is useful as it adds fulness to beers. As the colour becomes more intense the flavour becomes more acrid, but this should not be marked in well-made caramels of the most intense colour.

In England the colour is usually determined on a 0.1% solution in Lovibond's Tintometer using standard glasses of the 52 series and converting the value so found back to the original caramel. Further information can be obtained by using the yellow and red glasses. Grades with colours around 20,000, 30,000, 40,000 and 50,000 are available and are selected for use according to the purpose for which they are intended. For the drier, bitter beers, the most intensely coloured caramel may be used without communicating any acrid bitter flavour, since the quantity required is so small. For mild ales and stouts, one of the sweeter and less intensely coloured varieties is generally preferred. The fermentability of caramels usually decreases with increasing intensity of colour. Caramels are slightly acid in reaction, giving p_H values between 6 and 5. Acidities determined by titration and calculated as acetic acid may vary between 0.2 and 2.0%, generally increasing with the colour. Typical analyses of cane sugar and glucose caramels are given

in Table 91. The colours are expressed from Tintometer determinations with a 0.1% solution in a 1-inch cell and multiplied by 1000 to express the colour on the original sample. The percentage of iron should not exceed 0.01%. Caramel should not produce a precipitate in the course of 24 hours in bright beer coloured to resemble stout, neither should there be any loss of colour under these conditions in a week. Wort coloured in the same manner should show no loss during fermentation.

TABLE 91.—ANALYSES OF CARAMELS

	Crystal	Caramel syrups				
Colour, Tintometer 1-in. cell	32,000	26,000	32,000	40,000	50,000	
Extract, lb. per 224 lb. ..	80.5	65.0	64.0	63.0	62.0	
Water %	7.5	25.0	26.0	27.0	28.0	
Fermentable %	29.0	25.0	22.0	20.0	18.0	
Nitrogen %	2.0	2.0	2.5	3.0	3.5	
Ash %	0.5	0.5	0.5	0.5	0.5	
Iron %	0.007	0.004	0.004	0.005	0.005	

Caramel in weighed quantities may be added to the copper or small quantities of solution may be added to the beers at racking for final colour adjustment. In the latter case, solutions of standard tinctorial value are made in a manner similar to that adopted for primings and, after the customary excise charge on the bulk has been determined, the requisite small quantities are added to the beer. The colour should be standardised so that 1 oz. or other definite quantity produces a known increment in a barrel of beer.

SPECIFIC GRAVITY AND EXTRACT

(236) The Metric Unit of Volume.

So many principles of fundamental importance and everyday application in brewing can be made plain by a study of the methods of sugar analysis that they will be dealt with at this stage. At the outset, the apparently simple matter of the metric unit of volume must be referred to, as confusion has arisen through an error in the computation of the universally accepted standard kilogram and has only recently been rectified by use of a new term for the thousandth part of a litre. The standard kilogram is now simply the mass of a plain cylinder of platinum-iridium alloy, known as the International Prototype Kilogram, which

does not exactly comply with the original definition that the kilogram should be the mass of a quantity of water which, at its maximum density or at 4° C., occupies a cubic decimetre. Hence the litre, now defined as the volume of a kilogram of water at its maximum density, cannot be a cubic decimetre and a cubic centimetre cannot be the thousandth part of a litre. The error is very small as

$$1 \text{ litre} = 1000.028 \text{ cubic centimetres.}$$

Although the term cubic centimetre or cc. has become almost sanctified by long usage as the thousandth part of a litre, it has been replaced in the cause of accuracy by standardisation of the millilitre as the unit of volume by the British Standards Institution.⁴ The ml. is consequently now adopted by British makers in the graduation of calibrated glassware. 20° C. is the standard temperature for the graduation of flasks but some other temperature, such as 15° C. or 60° Fahr., is sometimes adopted. This makes an appreciable difference in the volume of the solution measured, since the latter generally expands differently from glass. The corrections given in Table 92 are applicable to a litre.

TABLE 92.—CORRECTIONS FOR VOLUMES OF WATER MEASURED IN
1,000 ML. FLASK

Temperature used ° C.	To obtain volume at 20° C.
5	+ 1.37 ml.
10	1.24
15	0.77
25	— 1.03
30	2.30

Confusion has been increased by the wide adoption of Mohr's system of graduation, based on the volume occupied at 17.5° C. by a quantity of water having an apparent weight in air of 1 kilogram. A litre of water at 60° Fahr. measured on this basis has a true volume of about 1002 cc., involving an error of 0.2% in analyses. Brown, Morris and Millar's tables, which are so largely used in sugar analyses, are based on measurements of this kind at 15.5° C. and the authors state that their results must be multiplied by 0.99802 to give grams per true cubic centimetre, meaning that one true litre of water weighs 998.02 grams in air with brass weights.

(237) Density and Specific Gravity.

Density is defined as mass per unit volume and is generally expressed as grams per millilitre for liquids. By mass may be understood weight *in vacuo*. The density of water at 20° C. is usually accepted as 0.99823 gram per millilitre, but variations due to the existence of heavy water are commensurate with the difference between the cc. and ml.

Specific gravity is the ratio between the mass of a substance occupying a given volume at t_1° and that of water occupying the same volume at t_2° . These temperatures are not necessarily the same and must therefore be stated, thus S 20°/4° C. or S 60°/60° Fahr.

In most laboratories the term specific gravity is used to denote the ratio between the weight in air, not the mass or weight *in vacuo*, of a given volume of the liquid and that of the same volume of water, using brass weights. This ignores the buoyancy in air of the bottle and its contents or the difference between the weights of air displaced by the specific gravity bottle and the brass weights.

Hydrometers are glass or brass instruments constructed with a bulb of spherical or cylindrical shape, surmounted by a graduated stem and weighted below to float vertically in a liquid at such a depth that the surface of the latter intersects the graduated stem. The hydrometer comes to equilibrium in the liquid in such a position that the surface intersects the stem when the volume of liquid displaced has a mass equal to that of the instrument. The point of intersection is therefore determined by the density of the liquid and the most direct method of graduation is in terms of density. This method has been standardised⁵ and is adopted in several industries. The position of equilibrium is affected to some extent by the surface tension of the liquid and the scale must be adjusted by trial in the liquid with which the hydrometer is to be used if great accuracy is required.

(238) Saccharometers.

Hydrometers constructed for use with sugar solutions are called Saccharometers, under which name they are known in breweries. British brewers are precluded by the Finance Act in force from adopting the density graduation for saccharometers, since the Act lays down that they must be scaled to read specific gravity at 60°/60° Fahr. as determined by weighing in air against brass weights. In order to avoid decimals the specific gravity thus defined is multiplied by 1000 and expressed as if the specific gravity of water was 1000. The term "degrees of gravity"

is used for the excess over 1000 found in this way. Thus a wort with a specific gravity of 1046·8 shows 46·8 degrees of gravity and saccharometers are scaled to show excess over 1000. Alternatively the scale may give the corresponding value in Brewers' pounds or may be graduated to read percentages of solid matter according to the Plato or Balling tables. The graduations must be reasonably spaced for accurate reading and either a number of saccharometers used or weights be added to sink the instrument in worts of greater density and to cover the range of gravities encountered in the brewery.

Accurate readings can only be obtained when the saccharometer is used at the temperature for which it was adjusted. Thus a correction of 0·3 has to be added to specific gravity, water = 1000, determined by a saccharometer scaled at 60°/60° Fahr., to give specific gravity at 17·5°/17·5° C. A correction of 0·7 must be added to convert to that at 20°/20° C. and a deduction of 0·9 made to convert to S 15°/4° C. A correction table is supplied with saccharometers in order that the true specific gravity may be calculated from readings at temperatures other than that for which the instrument was graduated. An approximate correction for saccharometers graduated at 60° Fahr. is 0·1 (water = 1000) to be added for each degree above 60° and subtracted for each degree below. The table used by the Excise for this purpose shows that the correction becomes rather greater than this with increasing specific gravity and higher temperatures. A thermometer is usually placed inside saccharometers scaled to read per cent. extract Plato or Balling.

Brass saccharometers constantly lose weight in use, so that they give a higher reading than they should. They must consequently be checked from time to time by means of sugar solutions, the specific gravity of which has been accurately determined by a specific gravity bottle. Correct readings can usually be obtained by adding a little solder to the weights to compensate for wear.

(239) Brewers' Pounds.

Before specific gravity was used in breweries, it was customary to express the strength of wort by the difference between the weight of one barrel (36 Imperial gallons) of the wort and that of a barrel of water. The latter weighs 360 lb. at 60° Fahr. This convention is still widely used in English breweries. The excess weight over 360 lb. is denoted by "Brewers' Pounds." Thus if a barrel of wort weighed 378 lb. it would be referred to as of 18 Brewers' pounds or simply as an 18 lb. wort, and saccharo-

meters are scaled to read accordingly at 60° Fahr. The relation between Brewers' pounds and specific gravity is given by

$$\text{Sp. gr.} = \frac{360 + \text{Brs.' lb.}}{360}$$

Thus a wort with a gravity of 18 Brewers' pounds, a barrel of which weighs 378 lb., has a specific gravity of $\frac{378}{360} = 1.050$ or, as usually written, 1050. To obtain "degrees of gravity" from Brewers' pounds it is thus necessary to divide the latter by 0.36 or to multiply degrees of gravity by 0.36 to obtain Brewers' pounds.

$$18 \text{ Brs.' lb.} \div 0.36 = 50^\circ \text{ of gravity.}$$

$$1040 \text{ sp. gr. or } 40^\circ \text{ of gravity} \times 0.36 = 14.4 \text{ Brs.' lb.}$$

(240) Extract.

The word "extract" is used with several significations in different breweries. In British breweries it refers to the materials and expresses the specific gravity of the wort or solution, either in degrees of gravity or Brewers' pounds, when unit volume is obtained from unit weight of materials. The unit of volume is the barrel of 36 Imperial gallons. The unit of weight is based on the old measurement of one quarter of malt. It is 336 lb. for malt or unmalted grain and 224 lb. for sugars, the latter weight being deemed equivalent in extract production to 336 lb. of malt.

It is usual to ascertain the extract of sugar by determining the specific gravity of a solution containing 10 grams in 100 ml. and calculating from it the specific gravity of a solution containing 224 lb. in a barrel (360 lb.) under the assumption that specific gravity and concentration are proportional. This assumption is shown in the next paragraph to be incorrect, but it gives results that are useful for commercial purposes. The calculations from the specific gravity of the 10% solution are as follows:—

$$\text{Extract (degrees of grav.)} = (\text{Sp. gr.} - 1000) \times \frac{10 \times 224}{360}$$

$$\begin{aligned} \text{Extract (Brs.' lb.)} &= (\text{Sp. gr.} - 1000) \times \frac{10 \times 224 \times 0.36}{360} \\ &= (\text{Sp. gr.} - 1000) \times 2.24 \end{aligned}$$

Thus if the 10% solution had a specific gravity of 1032.5, the extract per 224 lb. would be $32.5 \times 2.24 = 72.8$ Brs.' lb. or 202.2 degrees. The extract of sugar is generally expressed in Brewers' lb. per two cwt. but sometimes in Brewers' lb. per one cwt.

The specific gravity of wort collected in the fermenting vessel and its volume are taken as the basis for calculating the extract of materials used in a brew. Thus, if 50 barrels of wort of 1055 sp. gr. are collected from a brew in which 11 quarters of materials were used, the extract obtained from one quarter, often referred to as the extract of the brew, would be

$$\frac{50 \times 55}{11} = 250 \text{ degrees or } 250 \times 0.36 = 90 \text{ Brs.' lb.}$$

In most other countries extract means the weight in grams of dry solid matter in 100 grams of the wort, that is to say it is expressed as a percentage of the weight of the wort. In the brewhouse it is frequently expressed for convenience as a percentage on the volume of the wort, that is to say as grams per 100 ml. or in practice as kilograms per hectolitre, from which it can be calculated back to give the yield of the materials. The volume of wort is usually ascertained in the copper, immediately before turning out, an allowance of 4.0 or 4.2% being allowed for shrinkage from the boiling point to the temperature at which the extract is determined by the Plato or Balling saccharometer or to the temperature of collection in the fermenting vessel, and for loss in the copper, in the hops and cooler sludge. The extract yield of materials would thus be calculated from the formula

$$\text{Extract yield \%} = \frac{\text{Vol. of wort, litres} \times \text{Extract \% (on vol.)} \times 0.96}{\text{Weight of malt, kilog.}}$$

These two methods of expressing the "yield" of materials are not accurately convertible one into the other by any single factor, because the relation between specific gravity and concentration of sugar solutions varies at different concentrations and also because the saccharometers are standardised to read at different temperatures. An approximate conversion of specific gravity to extract % by weight can, however, be made by dividing the specific gravity less 1000 by 4, the specific gravity of water being expressed as 1000. This gives, also only approximately, the weight in grams of solids in 100 grams of wort or sugar solution.

(241) Solution Divisors.

Determination of the percentage of solids in sugar solutions and worts is essential for analytical purposes and is required in many countries for the assessment of duty. It is not practicable to evaporate a sugar solution to dryness and weigh the residue, but its percentage can be ascertained by dividing the difference between the specific gravity of the solution and that of water

by an appropriate figure, known as the "solution divisor." Solution divisors have consequently been determined with great care for a number of pure sugars.

The curves constructed by Brown, Morris and Millar⁶ from their determinations of the specific gravity of solutions of known concentration and reproduced in Fig. 39 show that the solution divisors are different for each sugar and vary at different concentrations, becoming less as the specific gravity of the solution increases. The figures themselves are not accepted as the most accurate now available and must in any case be corrected for use with modern graduated flasks, as they are based on a "reputed cc." and not a true cubic centimetre or millilitre, but they clearly express a principle of importance in analysis and of practical application in the brewery.

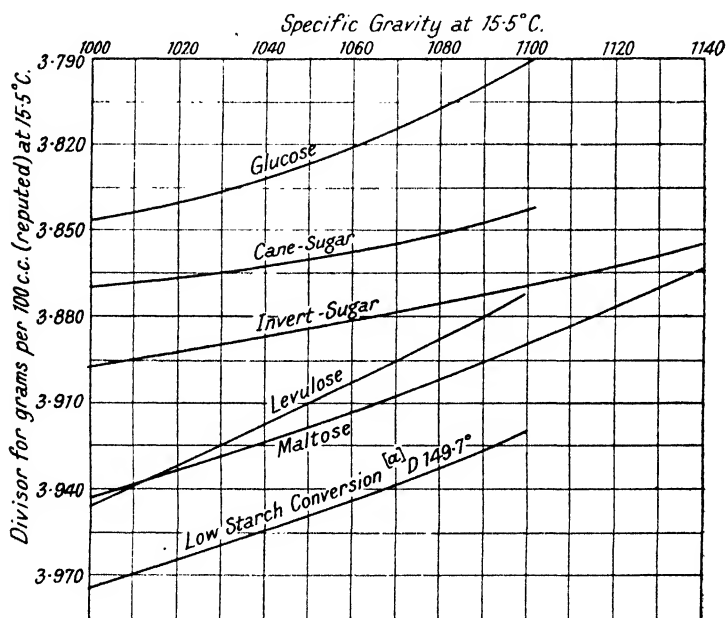


FIG. 39
SOLUTION DIVISORS FOR VARIOUS CARBOHYDRATES

To find the quantity of glucose, for example, in 100 "reputed cc." of a solution of known specific gravity, it is necessary to deduct the specific gravity of water and divide the remainder by the appropriate divisor found in the figure. Thus solutions of 1040 and 1080 sp. gr. would contain respectively per 100 reputed cc.

$$40 \div 3.832 = 10.4384 \text{ grams glucose, and}$$

$$80 \div 3.807 = 21.0189 \text{ grams glucose}$$

It will be noticed that the concentration of the solution and its specific gravity are not proportional. Hence a fixed divisor cannot be used, even for one particular sugar, at all gravities. If a glucose solution with specific gravity of 1080 be diluted to double volume, its specific gravity will not be 1040·0 but 1040·26. The dissolved sugar contracts on dilution, so that it takes rather more than one gallon of water to break down a gallon of the original solution to two gallons. Alternatively, it takes more than double the weight of sugar to double the specific gravity, keeping the volume constant. This gives the impression that the extract of the sugar is 0·56 lb. less at 1080 than at 1040. Discrepancies of this kind have given rise to unjustifiable complaints by brewers who have found the apparent extract of a sugar, when calculated from the specific gravity of primings solution, considerably lower than the guarantee based on analyses of a 10% solution. The following example illustrates this.

Ten grams of cane sugar dissolved in 100 ml. give a specific gravity of 1038·64, but 40 grams dissolved in the same volume give a specific gravity of 1152·69 and not 1154·56 as it would if specific gravity and concentration were proportional. Hence the extract if calculated from the concentrated solution would appear to be less than that determined in the laboratory.

Extract calculated from sp. gr. of 40% solution

$$= (1152·69 - 1000) \times 0·36 \times \frac{100}{40} \times \frac{224}{360} = 85·50 \text{ lb.}$$

Extract calculated from specific gravity of 10% solution

$$= (1038·64 - 1000) \times 0·36 \times \frac{100}{10} \times \frac{224}{360} = 86·55 \text{ lb.}$$

(SPECIFIC GRAVITIES FROM PLATO'S TABLES).

An analogous discrepancy in specific gravity arises when a gallon of primings at 1150 is added to a barrel of beer. The increase in gravity will be somewhat higher than might be expected.

TABLE 93.—SOLUTION DIVISORS FOR 10% SOLUTIONS OF SUGARS. (BROWN)

Sugar	Volume and Sp. Gr. at 15·5° C.	
	10 gms. in 100 reputed c.c.	10 gms. in 100 metric c.c.
Sucrose	3·863	3·871
Glucose	3·833	3·841
Fructose	3·918	3·926
Maltose	3·925	3·933

The cane sugar divisor 3.86 is very generally adopted for 10% solutions of other sugars and for brewery worts of about 1040 sp. gr. This is obviously inaccurate and can only give approximate estimates of the solids in solution. It is impossible to obtain an accurate universal divisor for worts, as they vary so much in composition and the solid matter in solution cannot be determined by evaporation without fear of decomposition. The ash in wort is another variable factor, the salts probably having a solution divisor of about 8. Different analysts have, in fact, adopted such divisors as 3.92, 3.95 or 4.0. The last is probably as accurate as the others and is most convenient for rapid calculation.

(242) Balling and Plato Tables.

Since it is impossible to draw up accurate tables for the relation between the specific gravity of worts and the percentage of dry solids dissolved therein, it has become necessary to adopt those constructed for pure cane sugar, despite the small error in their application to wort. The tables published by von Balling in 1813, giving the weight of cane sugar in 100 grams of solution corresponding with specific gravities determined at 17.5°/17.5° C., were until recently almost universally employed and are still official in Denmark, the United States and some other countries. "Balling degrees" is consequently often colloquially applied to percentages of extract in worts, even where newer and more accurate tables have been adopted.

In view of slight inaccuracies in the Balling Tables, the German Law of July 26th, 1918, governing the taxation of beer, prescribed that the extract content or percentage of dry solids in wort should be based on density determinations at 20°/4° C. and on the more accurate tables published by Dr. F. Plato in the Report of the *Normal-Eichungskommission* of 1900, which also show the cane sugar percentages as grams per 100 grams of solution. For convenience in laboratories, specific gravity is usually determined with brass weights in air at 20°/20° C. or in some cases at 17.5°/17.5° C. It was consequently necessary to have tables calculated accordingly for use in breweries. These give the true specific gravity at 20°/4° C., the corresponding extract % or saccharometer reading and the "laboratory quotient" or specific gravity either at 20°/20° C.⁷ or at 17.5°/17.5° C.⁸ Corresponding tables are attached to the American malt analysis publication⁹ and others have been constructed by Krause¹⁰ for the relation between Balling and Plato extracts.

These tables are known as Plato Tables and the extracts

are referred to as % Plato. They have been adopted for laboratory use in America and are gradually superseding the Balling Tables. In calculating them from the official table, it was necessary to take into consideration the difference between the density of water at 20° and 4° C. and also the buoyancy of air, for which an average value of 0.00121 was taken by Goldiner and Klemann. From these

$$\begin{aligned} S_{20^\circ/4^\circ} &= S_{20^\circ/20^\circ} (0.99823 - 0.00121) + 0.00121 \\ &= S_{20^\circ/20^\circ} \times 0.99702 + 0.00121 \end{aligned}$$

A specific gravity of 1.03083 at 20°/20° would thus represent a density of 1.02897 at 20°/4°, which corresponds to a cane sugar percentage of 7.76 grams per 100 grams solution. This would be the extract percentage corresponding to 1.03083.

A cane sugar solution containing 10 grams of sugar in 100 grams of solution has a specific gravity, 20°/20° C., of 1.04003. 20 grams sugar in 100 grams gives a specific gravity of 1.08298 and 30 grams in 100 grams a specific gravity of 1.12904.

The Brix and Baumé tables are also used for cane sugar solutions. The former is based on the Balling tables and gives grams in 100 grams from specific gravities at 20°/20° C. The Baumé table is based on salt solutions and, as accepted by the American Bureau of Standards for sugar solutions, is based on the specific gravity tables of Plato at 20° C. and a modulus of 145, so that

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{sp. gr.}}$$

(243) Use of Refractometers.

The refractive index of sugar solutions has been found to afford a reliable indication of the dry weight of solids in the solution. Refractometers by several makers can be used for the purpose, the refractive index of 1% sugar solutions being 1.3335, that of 10% solutions 1.3469, while 20% solutions read 1.3627 at 28°C. The immersion refractometer is particularly convenient and is successfully applied in the determination of the original gravity of beers. The scale is divided into 110 arbitrary divisions corresponding with refractive indices from 1.325 to 1.367, distilled water reading 15.0 at 17.5° C.

Determination of the original gravity of beer from the refractive index and specific gravity is much more rapid than the official distillation method and accurate to about 1 degree of original gravity. It may also be applied to acid beers, as the refractive indices of solutions of alcohol and of alcohol and acetic

acid in equimolecular proportions are nearly the same. The method depends on the fact that the increase in refractive index produced by both alcohol and unfermented extract in beer and the decrease and increase in specific gravity produced by alcohol and extract, respectively, are proportional to their concentrations. Hence it is possible to construct equations from which the percentages of alcohol and unfermented extract can be calculated. The alcohol percentage found is then converted to specific gravity from such tables as those of Simmons. This specific gravity deducted from 1,000 gives the "Spirit indication" from which the specific gravity which would be given by fermented extract is ascertained from the official original gravity tables. This added to the specific gravity due to unfermented extract, calculated from the percentage of the latter, gives the original gravity of the beer. In the following equations, A and E represent the percentages of alcohol and extract respectively, Z_1 and Z_2 are experimentally determined constants for the increase of refractive index produced by 1% of extract and alcohol, while Z_3 and Z_4 represent the increase and decrease of specific gravity due to 1% of extract and alcohol, respectively.

$$\text{Refractive index, } R = 1 + Z_1 E + Z_2 A$$

$$\text{Specific gravity, } S = 1 + Z_3 E - Z_4 A$$

OPTICAL ACTIVITY AND REDUCING POWER

(244) Polarimetry.

One of the most striking properties of sugars (see Section 109) and many other substances is the power of rotating the plane of polarisation of plane polarised light during transmission through their solutions. A working idea of what this means and of its applications in the analysis of sugars and wort can be gathered from a few simple experiments. A beam of light passing into calcite and certain other crystals is not only bent or refracted in the ordinary way, as in glass, but is divided into two components, whereby two images of the light source or of an object seen through the crystal become visible. The light rays forming these are referred to as ordinary and extraordinary rays, respectively. Their vibrations are in planes which are mutually perpendicular and both are said to be plane polarised. Nicol (1828) found that one of these rays could be suppressed by cutting through a rhombohedral crystal of Iceland spar, a very transparent form of calcite, from corner to corner through a plane CKFL, at right angles to a principal section AFHC, and cementing the two halves in their original position with Canada balsam,

as shown in Fig. 40, N. This discovery made possible the construction of accurate polarimeters. Various modifications have been made in the original Nicol's prism, but the principle remains the same. The figure shows a ray, I, incident on the end face of a Nicol and doubly refracted to form an Ordinary ray, O, and an Extraordinary ray, E. The former is totally reflected at the Canada balsam and, passing out of the side of the prism, is absorbed at its blackened surface. The extraordinary ray passes through the cemented surfaces and emerges from the other end face of the crystal. The courses of the two rays are accounted for by the different refractive indices of Canada balsam and the two rays. That of Canada balsam is 1.55, intermediate between those of the ordinary and extraordinary rays in Iceland spar. The former is 1.658, while the latter varies from 1.486, when the ray is perpendicular to the optic axis, to a value approaching that of the ordinary ray as it comes closer to the optic axis. The angle of incidence of the ray I is consequently restricted within certain limits to allow of the passage of the extraordinary ray through the prism.

A source of light viewed through the prism appears quite normal, though reduced in brilliance, in whatever position the Nicol is placed. If two Nicols are placed symmetrically at the ends of a tube, the light source can still be seen through them, but if that nearer the eye is rotated in the tube, the intensity of the transmitted light diminishes until it is extinguished when the prism has been turned through 90° either way. That is when the axes of the two Nicols are crossed. Light emerging from the first Nicol appears to be different from the original incident light, since it does not pass through the second when their axes are crossed. An explanation can be found in the influence of the crystal on the direction of light vibrations. These are transverse to the path of the ray in which they occur, but the direction of vibration in the incident ray is constantly changing. The crystalline structure of Iceland spar may be supposed to force the vibrations of the ordinary and extraordinary rays to take place in planes which are mutually perpendicular. It is this restriction of vibrations to definite planes that is referred to as plane polarisation. Both rays are plane polarised in planes at right angles to their respective planes of vibration, and the prism that brings this about is known as a polariser. The vibrations of the emerging extraordinary ray are in a plane parallel to AC, and those of the ordinary ray in a plane parallel to BD. The former when incident on the second Nicol, placed symmetrically with respect to the polariser, are parallel to planes in which alone the other Nicol transmits vibrations.

The light is consequently transmitted with maximum intensity, but no light can pass when the prism is turned so that these planes are at right angles to their original position.

If, now, a tube of sugar solution is placed between the crossed Nicols, it will be observed that light can once more pass through them both. The sugar is optically active and rotates the plane of polarisation or, rather, the plane of vibration to which the so-called plane of polarisation is at right angles, clockwise or counter-clockwise or, as it is styled, to right or left according as the sugar is dextro- or lævo-rotatory. It will then be found necessary to turn the movable prism to right or left to extinguish the transmission of light. This arrangement of a fixed polariser and a movable Nicol represents the simplest form of polarimeter, or instrument for measuring the angle of rotation caused by the sugar solution. The angle through which the movable prism is turned to quench the light is equivalent to the rotation produced by the sugar. This prism is therefore called the analyser and its movement is measured by an attached arm carrying a vernier round a circular scale divided in degrees of arc. The angle of rotation, measured in degrees of arc, produced by one decimetre length of solution, divided by the weight of the active substance in grams per ml. is its rotatory power. This calculated back to 100 grams per 100 ml. gives the rotatory power of the substance or substances in solution. Since this is specific for each sugar and varies with the depth of solution, at moderate dilutions, a polarimeter can be used for determining the concentration of a sugar, the specific rotatory power of which is known, by placing a tube of solution, 100 or 200 mm. in length, between the crossed Nicols and ascertaining the rotation produced by measuring the angle through which it is necessary to turn the analyser to right or left, according as the sugar is dextro- or lævo-rotatory, to produce extinction of light. Alternatively, it can be used to determine the identity of a pure sugar in a solution of known concentration.

The angles of rotation produced by sugar in the component rays of white light differ, increasing approximately inversely as the square of the wave-lengths. This effect is referred to as rotatory dispersion. Consequently it is impossible to obtain complete extinction of light by the analyser, unless monochromatic light is used. The incandescent vapour of sodium salts in a Bunsen flame has been most generally used for this purpose. The sodium light is, however, not strictly monochromatic, but consists of two bright yellow lines, D_1 and D_2 , with effective wave-lengths varying between λ 589.3 and 589.6 $\mu\mu$ for different illuminants. In some cases the green

light of incandescent mercury, with a wave-length of λ 546.1 $\mu\mu$, is to be preferred for very accurate work. The lack of visual intensity in these sources of monochromatic light was a serious handicap in polarimetry with dark coloured solutions, but the difficulty has been overcome by the electric sodium lamp which has an intrinsic brilliance equal to that of a 60-watt gas-filled lamp.

A more serious difficulty with the simple arrangement of two Nicols described, arises from the fact that the position of light extinction cannot be found with sufficient exactness for accurate measurements. Special devices are consequently incorporated in polarimeters to divide the field of view into two or, sometimes, three parts which are brought to equal brilliance by rotating the analyser. This half-shadow effect can be produced, but not very sharply, by placing near the polariser a plate of glass on to which a half disc of quartz, cut parallel to its axis, is cemented. Light passing through the glass is stopped by the crossed analyser, which passes to a considerable extent that coming through the quartz. Half the field of view is consequently more brilliantly illuminated than the other half. There is one point of rotation at which the intensity of light is equal on both halves of the field and this provides for a much more accurate setting than reliance on maximum darkness. Any means by which the analyser can be consistently placed in a definite angular position with regard to the plane of polarisation of the original light can be used for measuring rotation. Specially designed polarising systems are generally used in modern polarimeters to produce the half-shadow effect. The Lippich polariser, for instance, consists of a large square-ended prism with a second small Nicol behind, covering half its field and with its principal section inclined at a small angle to that of the principal prism. With this arrangement light from both sections of the field is not simultaneously extinguished. Bellingham and Stanley employ a polarising system constructed from two rhombs of Iceland spar. One side of each is ground to a certain extent and the two parts are held in contact without any cement, as shown at P in Fig. 40. These prisms are securely mounted in a tube protected from dust by the condensing lens at one end and a glass window at the other, but are removable as a unit from the polarimeter.

(245) Saccharimeters.

Quartz plates cut perpendicular to the axis of the crystal have the property of rotating the plane of polarisation in a similar manner to sugar. Some crystals produce right-handed and others left-handed rotation, to a degree varying with their

thickness. It is consequently possible to insert a quartz plate between a tube of sugar solution and the analyser of a polari-

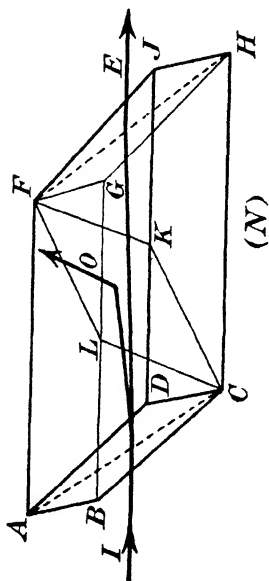
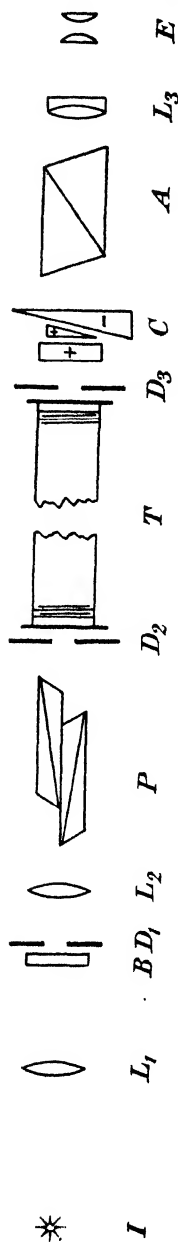


FIG. 40
DIAGRAM OF A SACHARMETER AND NICOL'S PRISM

meter that will exactly compensate for the rotation produced by the sugar and restore extinction of light with crossed Nicols.

In addition, the rotatory dispersion of quartz is almost identical with that of cane sugar, within the visible spectrum of white light. This implies that a quartz plate which annuls the rotation produced by cane sugar with light of one wave-length will also compensate for others, and almost complete extinction can be produced with crossed Nicols for white light. The small difference between rotatory dispersions of quartz and cane sugar is greatest with light of shortest wave-length, which can be eliminated from white light by interposing between the lamp and analyser a flat-sided cell, 1.5 cm. in width, containing 6% solution of potassium bichromate. An equivalent solid light filter is generally used in modern instruments.

Advantage is taken of these properties of quartz in the construction of polarimeters particularly adapted to the analysis of cane sugar. These instruments, known as Saccharimeters, are the most suitable type of polarimeter for analysis of wort, the rotatory dispersion of which is very close to that of cane sugar solutions. The convenience and brilliance of white light greatly recommends them. They do not directly measure the angle of rotation produced by sugar solutions, measurements being based on the thickness of quartz of opposite rotatory power required to annul the rotation produced by the sugar. For this purpose quartz compensating systems are available, consisting essentially of a wedge of quartz which can be moved into such a position that the two halves of the field of view are equally illuminated. The wedge is cut in such a way that its lateral movement is exactly proportional to its thickness at any point. This single wedge is replaced in saccharimeters by systems consisting of two or more wedges, with or without a parallel-sided plate of quartz. A fixed and movable wedge, both of lævo-quartz, can, for instance, be combined with a dextro-quartz plate, the rotation of which they exactly neutralise at the zero point. The rotation produced by cane sugar can then be annulled by increasing the combined thickness of the wedges.

The construction of a saccharimeter is diagrammatically illustrated in Fig. 40. The analyser and polariser are fixed with their axes crossed. The polariser, P, represents that of Bellingham and Stanley and gives the half-shadow effect. The quartz compensating system, C, consists, in this case, of a large moving wedge of left-handed quartz, adjacent to the analyser. Behind this, there is a short fixed wedge of right-handed quartz. These two wedges are so placed that, when in position, they exactly neutralise each other for angle and the crystallographic axis is exactly coincident with the optical axis of the instrument. Behind the short fixed wedge is a parallel-sided plate of right-handed

quartz of such a thickness that, at the zero point, it exactly compensates for the combined thickness of the left-hand moving wedge and the right-hand fixed wedge. The large wedge is moved laterally across the fixed wedge by means of a suitable mechanism and milled head. Its mounting carries a scale, adjacent to a fixed vernier, which is read by means of a magnifying combination of lenses. The zero point is marked with the moving wedge in such a position that the two halves of the field of vision are equally illuminated. I represents the illuminant, which may be a pearl electric lamp. The lens, L_1 , focusses an image of the illuminant on the diaphragm D_1 , which is at the focus of the condensing lens L_2 , so that parallel light traverses the instrument. D_2 and D_3 are other diaphragms to cut out stray light. L_3 and the eye-piece E form a telescope focussed on P. The half-shadow field is examined through these and set to even illumination by moving the large wedge when the sugar solution, in the tube T, is in position in the trough connecting the optical parts of the instrument. The scale is read by reflected light from I. B is the light filter. The end pieces of the solution tube must only be lightly screwed into position, as strain on the glass discs produces polarising effects which cause incorrect readings.

Saccharimeter scales are now generally graduated according to the International sugar scale, giving a reading of 100 divisions at 20° C. with a 2-dm. tube of cane sugar solution, containing 26 grams of cane sugar dissolved in water and made up to 100 ml. at 20° C. The zero point being fixed as previously indicated, the point on the scale at which equal illumination is obtained with 2 dm. of the normal sugar solution is marked and the intervening space graduated in 100 equal divisions. The scale is usually continued up to 130 and down to -30 to give control over all right- and left-handed sugars. Readings on this scale multiplied by 0.26 give percentages of cane sugar, when solutions of the normal concentration, 26 grams per 100 ml., are examined in a 2-decimetre tube at 20° C. They can be converted into angular degrees of rotation by multiplying by 0.346.

Lack of homogeneity in the quartz used in compensating systems is liable to give rise to small errors in readings. Bellingham and Stanley have found it possible entirely to eliminate the quartz compensating system by taking advantage of the brilliance of the electric sodium lamp. The instrument, which must be used with monochromatic light, contains a standard polarising and analysing system, but the quartz wedges and scale are replaced by a glass circle and vernier to measure the rotation of the analyser. The sugar scale is etched on the circle, with which the glass vernier is in close contact.

(246) Optical Activity of Sugars.

The specific rotatory power of a substance is designated by $[\alpha]_D$, in which α represents the angle of rotation produced by passage of the polarised light through a tube 1 dm. in length containing 1 gram of the substance in 1 ml. and D indicates that the sodium light was used. It is calculated from the observed rotation in a polarimeter, α_o , by the formula

$$[\alpha]_D = \frac{\alpha_o \times 100}{l \times c}$$

in which l is the length of the tube and c the weight of substance in 100 ml. In sugar analysis c must generally be calculated from the specific gravity, for which purpose the conventional divisor 3.86 is used. The specific rotatory power then becomes

$$[\alpha]_{D,\dots} = \frac{\alpha_o \times 100}{l \times \frac{d}{3.86}}$$

in which d = sp. gr. — 1000.

Readings obtained in a saccharimeter must be converted to angular degrees of rotation to give specific rotatory powers in terms of $[\alpha]_D$. For this purpose they are multiplied by a factor which differs slightly for different sugars, but 0.346 is sufficiently accurate for general use. The angle obtained in this way is then substituted for α_o in the formula given above. Solutions of about 10% concentration are used. The tubes are usually 1 or 2 dm. in length and hence l becomes 1 or 2 as the case may be. The specific rotatory power may be positive or negative, according as the sugar is dextro- or lævo-rotatory, the appropriate sign being added in the latter case. It varies with the temperature of the solution, and must therefore be determined under standard conditions. This is at 20° C. Great precision in regard to temperature is not required in ordinary analyses of worts and brewing sugars, since the errors involved in small deviations from the standard are slight, though they may become appreciable in the case of fructose and invert sugar. The $[\alpha]_D$ of fructose also varies with the concentration, from -89.4° at 5% to -93.3° in 20% solutions. It will be noticed how important it is to have an accurate sugar divisor for determining the optical constants of sugars with precision.

All sugar solutions should be boiled for a few minutes to stabilise the optical activity before the reading is taken, on account of mutarotation (see Section 109). In the case of glucose the angle falls on boiling. In that of maltose it rises. The optical activity of

stable fructose varies considerably with the temperature, becoming less negative as the temperature rises, until at 87.3° C. it is equal and opposite to that of glucose, so that a solution of invert sugar is optically inactive at this temperature. Cane sugar does not show muta-rotation. The optical constants for some of the more important sugars are given in Table 94.

TABLE 94.—OPTICAL CONSTANTS FOR SOME SUGARS

	Specific rotation $[\alpha]_D$			Saccharimeter reading in 1-dm. tube, 1% solution
	Stable form	α -form	β -form	
Glucose	52.8	113.4	19	1.525
Galactose	80.5	133.0	52	2.325
Mannose	14.6	34.0	— 17	0.422
Fructose	— 92.0	— 21.0	—133.5	— 2.655
Invert sugar ..	— 19.6	—	—	— 0.565
Lactose	55.3	90.0	35.0	1.597
Maltose	138.0	168	118	3.985
Cane sugar ..	66.5	—	—	1.92

Two other scales have been widely used. The German or Ventzke scale in use up to 1900, on which the 100 reading is fixed by that given at 17.5° C. by 26.048 grams sucrose in 100 Mohr cc. at 17.5° C. The readings are comparable with those of the International scale. On the French scale 16.29 grams of sugar in 100 true cc. at 20° C. read 100 in a 2-dm. tube. 1° on this scale is equivalent to 0.62516 on the International sugar scale.

Normal weights of other sugars, giving readings in a 2-dm. tube of 100 or — 100 on the International sugar scale when their solutions are made up to 100 ml. at 20° C., are given in Table 95.

TABLE 95.—NORMAL WEIGHTS OF SUGARS

Sugar	Grams per 100 ml.
Cane sugar	26.000
Glucose	32.248
Lactose	32.857
Maltose	12.474
Raffinose	16.507
Fructose	18.592
Invert sugar	86.450

The optical rotation of a sugar solution of known concentration provides a useful method for identifying the sugar by comparison

of the $[\alpha]_D$ with the known constants of sugars. It may also be used for the quantitative estimation of known sugars. The Clerget method for determining the quantity of cane sugar is an example. This is based on the fact that when cane sugar is inverted the invert sugar produced has a known negative rotatory power. If the method is to be applied to a raw sugar, 26 grams of the latter are dissolved in 100 ml. and, if necessary, boiled and clarified with lead acetate. If the sugar were pure cane sugar the reading in a 2-dm. tube in a saccharimeter would be 100. The reading of a raw sugar, reduced by moisture, invert sugar and other impurities is known as its polarisation and should be over 90 for a good brown sugar used in brewing. To determine the percentage of cane sugar in it, 50 ml. of the solution, freed from lead by addition of anhydrous sodium carbonate, is placed in a 100 ml. flask, 5 ml. of strong HCl with 25 ml. of water added and the flask placed in a water bath at 70° C. for 10 minutes, cooled to 20° C., made up to 100 ml. and polarised at 20° C. The percentage of cane sugar is calculated from the following formula, in which P is the reading before inversion and I the reading after inversion multiplied by 2, the readings for pure cane sugar falling from 100 to - 32.66 after inversion,

$$S = \frac{100(P - I)}{132.66}$$

Cane sugar may be similarly determined in 100 ml. of a 10% solution of invert sugar, for example, by inverting with 5 ml. concentrated HCl, making up the volume to 110 ml. after inversion, and taking the reading in a 2-dm. tube. The reading is corrected for dilution by multiplying by 11/10 and the percentage of cane sugar is given by dividing the difference between the original reading and that after inversion by 0.51.

(247) Reducing Power of Sugars.

Sugars may be differentiated as reducing and non-reducing, according as they do or do not reduce cupric ions to cuprous and precipitate the latter as cuprous oxide when boiled with alkaline solutions of cupric salts. Glucose, fructose, maltose, lactose and invert sugar are reducing sugars, while cane sugar does not reduce alkaline copper solutions. The reactions between the sugars and cupric salts are not strictly quantitative unless the experimental conditions are very rigidly standardised, when the quantity of cupric salt reduced is characteristic of the particular sugar. It has, however, been possible to devise accurate gravimetric and volumetric analytical methods, which are widely used in the

analysis of sugars and wort. The gravimetric methods depend on determination of the weight of cuprous oxide precipitated by a measured quantity of the sugar solution. The cuprous oxide is usually oxidised to CuO and weighed as such. In volumetric analyses the quantity of sugar present is determined from the volume of its solution required completely to reduce a measured quantity of standard alkaline cupric salt solution when boiled for a definite time.

Fehling's solution, containing copper sulphate, Rochelle salt and caustic soda in definite concentrations, is most commonly used in both gravimetric and volumetric analyses. The relation between the quantity of copper reduced and that of sugar present is given in tables which have been constructed for each individual reducing sugar and for use with the particular method of analysis employed, and it must be noted that these tables only apply when the conditions of experiment on which they were based are strictly adhered to.

The cupric reducing power of sugars was expressed by O'Sullivan in terms of the weight of copper reduced by unit weight of glucose, taken as 100. He found that 1 gram of glucose reduced 2.205 grams of CuO and expressed the reducing power of another sugar which reduced half this quantity as $K = 50$ or $\kappa = 50$. If the tables compiled by Brown, Morris and Millar and other authors are compared, it will be found that their values for glucose do not agree with one another or with that given by O'Sullivan. The relative values for different sugars vary quite considerably with different analytical technique, and K thus loses much of its value as a characteristic of the sugars and can only be taken as approximate, unless the conditions of experiment are very clearly stated.

The corresponding relative values based on maltose and referred to as R are more frequently used, particularly for worts and starch conversion products, but similar restrictions apply to their general application. The figures in Table 96 illustrate these points. The relative reducing powers for gravimetric analyses (A) and the equivalents of the sugars for 200 mgm. CuO are based on Brown, Morris and Millar's tables for glucose, fructose, invert sugar and maltose, with Dobie's figures for lactose. The figures for volumetric analyses are from Lane and Eynon's tables, when 25 ml. of sugar solution is required to reduce 10 ml. of Fehling's solution.

It will be observed that a determination based on reduction of Fehling's solution gives no indication of the nature of the substance causing the reduction. It is consequently usual in

analyses of mixtures of sugars to express the weight of reducing sugars present in terms of one of them by converting the weight of CuO reduced into that sugar. The methods of analysis are completely empirical, the results varying with the technique employed and can only be interpreted by means of tables constructed for each individual reducing sugar under the conditions specified.

TABLE 96.—RELATIVE REDUCING POWERS OF ANHYDROUS SUGARS

	Glucose	Fructose	Invert	Maltose	Lactose
(a) Mgm. sugar = 200 mgm. CuO ..	77.8	85.2	81.5	145.3	113.7
Relative reducing power ..	100	91.3	95.4	53.5	68.4
(b) Mgm. sugar = 10 ml. Fehling ..	49.8	52.8	51.2	76.4	64.5
Relative reducing power ..	100	94.3	97.3	65.2	77.2

(248) Analyses of Sugar Mixtures.

The analyses of mixtures of sugars tend to become very complicated unless it is possible to determine one of them by some special method, such as the percentage of cane sugar by inversion. It is in many cases necessary to employ as many different analytical processes as there are sugars, constructing simultaneous equations from the results. Thus, if three sugars were present, it might be possible to construct three equations with x , y and z representing their respective quantities.

$$(1) \quad x + y + z = \text{total sugars.}$$

$$(2) \quad ax + by + cz = \text{reducing sugars as glucose.}$$

$$(3) \quad lx + my + nz = [\alpha]_D$$

The total sugar would be determined from the specific gravity by means of the divisor 3.86, allowance being made for specific gravity due to the ash, which may be assumed to have a solution divisor of 8, by subtracting ash % $\times 2.07$ from the specific gravity before using the divisor 3.86. The total reducing sugar is computed from the glucose table, a , b and c representing the relative reducing powers of the three sugars, while l , m and n are their optical activities.

(249) Summary.

The sugars used in brewing are derived almost exclusively from the sugar cane or maize starch. Cane sugar is used as such,

either as refined sugar or in the form of high grade raw sugars which are appreciated on account of their luscious flavour. In addition, very full flavoured and readily fermentable brewing sugars are made by inversion of cane sugar. These are known as invert sugar and are extensively used in the copper or as primings.

Starch sugars are manufactured by acid conversion of purified maize starch and, in the form of glucose and partly converted syrups, are useful either in the copper or as primings, some of them because they are only slowly or partly fermentable. These are drier in flavour than raw cane sugar or invert sugars, but full-flavoured mixtures are made with the latter sugars for copper and priming purposes. Caramels are made either from cane sugar or glucose by controlled heating, usually in presence of ammonium salts.

Three important and characteristic properties of which use is made in the analysis of sugars and which have other applications in brewing are :—

- (1) Solution density.
- (2) Optical rotatory power.
- (3) Cupric reducing power.

The specific gravity of a sugar solution is not exactly proportional to its concentration, varying with the nature of the sugar and its percentage. As a result different divisors are required to determine the sugar content of a solution from its specific gravity. The divisor 3.86, appropriate to 10% solutions of cane sugar, is conventionally used in sugar analysis. For accuracy it is necessary to make use of tables showing the relation between specific gravity and sugar concentration. The most accurate tables available are those of Plato for cane sugar percentages by weight, which are displacing those of Balling for brewery use. They are assumed to give the weight of dry wort solids in 100 grams of wort from the specific gravity at 20° C.

The optical rotatory power of sugars is specific and can be applied by means of the polarimeter to sugar analysis. The cupric reducing power of many sugars can also be used for distinguishing one from another and for their quantitative determination. It, however, varies for each reducing sugar according to the conditions of experiment and analyses must be based on tables constructed to show the relation between sugar quantity and copper reduced under strictly specified conditions. Cane sugar does not reduce Fehling's solution.

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HOPS

CHAPTER XV

CULTIVATION AND TREATMENT OF HOPS

HOPS AND THEIR PRODUCTION

(250) Use of Hops.

A large number of plants and plant products have in the past been used to flavour beer or to communicate properties thought to be beneficial to health. The point of view of brewers, after the idea that hops were a “noxious weed” had been overcome, may be judged from a quotation from Tryon’s *A New Art of Brewing Beer*, of 1691. “Here give me leave to tell you that there are a great number of brave Herbs and Vegetations that will do the business in brewing as well as Hops and for many constitutions much better ; for ’tis Custom more than real Virtues that renders Hops of general Use and Esteem ; they are an excellent Herb and would be much better, if they were or could be dried in the Sun. Penny Royal and Balsam are noble Herbs and of excellent use in Beer and Ale ; they naturally raise and cheer the drooping Spirits, and open and cleanse the passages after a friendly way, and with a mild operation. And also they add great strength and frequency, and make brave well-tasted Drink, good to prevent and cure all, or most of those Diseases which the wise Ancients have appropriated that Herb unto. The like is to be understood of Mint, Tansie, Wormwood, Broom, Carduus, Centaury, Eye-bright, Betony, Sage, Dandelion, and good Hay ; also many others according to their Natures and Qualities, and for those Diseases to which they are respectively appropriated.”

As to hops themselves, “there is in them a most excellent glance or friendly opening quality, more especially if they were dried in the Sun, which is to be preferred before the Host or Kill ; for the spirituous parts of this Plant is so nice, that it cannot indure any violent heat without prejudice to its fine Virtues. Hops naturally purges powerfully by Urine, if prepared and used with understanding, so that they are unjustly charged to breed the Stone, for on the contrary, they are a special Remedy against it. Gentle infusion methods will naturally and without violence to Nature, extract or draw forth all that is desired in Hops, but ’tis true, it will not rouzen or infect your Liquor with their original

harsh, bitter, fulsome, keen hot Properties, which too many, for want of distinguishing the Principles of Nature, call Virtue and Strength ; indeed Strength and Fierceness it is, but far from Virtue in respect of Humane Bodies. Which evil Properties in every thing are the more drawn forth and increased by overmuch boiling, especially in Herbs and Vegetations which have been already firmented and digested by the influence of the Sun and Elements, whereby the gross phlegmy Parts are opened and the Spirits set upon the wing ready to come forth at any gentle Summons."

Though the medicinal properties of hops may now to a large extent be overlooked, it is generally agreed that they add to the dietetic properties of beer and impart the most pleasant flavour and aroma to fermented malt liquors, increasing their refreshing quality and stimulating digestion. So pre-eminent have they proved in these respects that hops have long ago completely displaced all their competitors, their structure and constituents admirably fulfilling all requirements. Among these are the need for a preservative agent capable of protecting beer from the growth of bacteria and for a wort-clarifying agent. No substance is known to meet the need of a preservative so well as certain constituents of the resins of hops, which ensure the soundness and stability of beer, without danger to health or detriment to the yeast. The small percentage of tannins in hops materially assists the precipitation of proteins during copper boiling and the extracted cones are themselves useful as a filter to clarify the wort, which has previously been sterilised by heat with the assistance of the slight acidity imparted by the hops. The colloidal properties of the resins or certain of their constituents are also believed to have an important influence on foam formation in beer. The useful constituents of hops, referred to incidentally in this chapter, are more fully described in the next.

(251) The Hop Plant.

Some acquaintance with the cultivation of hops, the development of the cones and their subsequent treatment is very helpful in appraising their brewing value and the influence of varying climatic conditions on their characteristics. The plant itself is botanically allied to the hemp or *Canabacæ*, but is placed by Engler and Prantl in the order *Moraceæ*, which includes the mulberry, and, by Bentham and Hooker, with the nettles in the closely allied *Urticaceæ*. Both these orders belong to the cohort *Urticales*. Three species, distinguished by differences in the formation of the leaf and stipules, are included in the genus *Humulus*. These are *H. lupulus*, the common hop of Europe, *H. americanus*, indigenous



FIG. 41
MALE FLOWER AND FEMALE STROBILE OF HOP

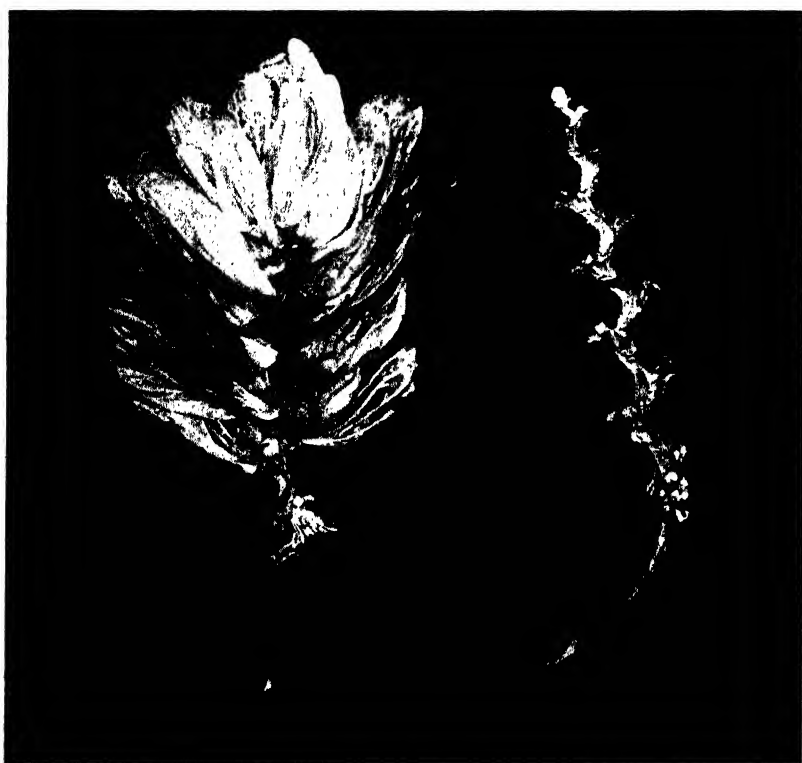


FIG. 42
PARTIALLY DISSECTED DRIED HOP CONE AND STRIG

Facing page 337]

to the west coast of America from British Columbia to New Mexico, and *H. japonicus*, found in the East. The last has decorative leaves but no brewing value, while the European and American species produce cones with distinctive aromas and, particularly the former, include many varieties or strains with characteristic differences.

The hop is dicæcious, bearing male and female flowers on different plants, and fertilisation is effected by air-borne pollen, which is frequently blown over considerable distances from one plant to another. Hence the necessity for removal of all wild as well as cultivated male plants found growing in the neighbourhood of gardens in which pollination is to be prevented. Hops are propagated by means of cuttings which, in England, are usually taken from the lowest six to eight inches of the stem of the previous season, attached to the rootstock in which reserve food material has accumulated. In America cuttings are taken from underground runners provided with rootlets. Straps grown one year in a field form sets which are planted in the hop garden between November and March of the following year. In England the bine does not come into full bearing until the third year but in America a good crop is frequently obtained in the second.

It is only exceptionally that established races have been raised from seed. The Fuggle is a notable instance, being said to have originated from seed planted at Horsmonden, Kent, in 1861. Raising hops from seed is not commercially feasible on account of the impossibility of distinguishing the variety of the male plant or knowing what its heritable characteristics will be and the sex of the seedlings. Different strains might appear together, ripening at different times and requiring different cultivation, while a large percentage of the seeds do not grow and some yield nothing better than wild hops. Raising from seed is almost exclusively confined to breeding new varieties at Scientific Stations, such as that of Wye College in Kent. It demands long-continued testing and weeding out of the progeny, before strains of promise can be selected and grown up for more thorough trials, while four to five years is required to produce a full crop from seed.

(252) The Cone.

The inflorescence of the female hop forms the "burr" and develops into the hop cone. In its early stages the latter carries a number of very small bracts and bracteoles, while the stigmata surmounting the ovaries give it the appearance referred to as "brush." About the middle of July the flower may be fertilised by pollen blown from male plants in the vicinity, when the brush-

like stigmas shrivel and the hop begins to develop. The period of brush is very critical in districts in which the hop is liable to be attacked by mould, as the damage done leads to complete destruction of the cone, while later attacks may cause only partial damage. The hop cone is formed even without fertilisation but its development is then delayed and, consequently, fertilisation tends to safety in damp weather.

The plant is said to come into hop when the strobile commences to develop. The axis of the cone is known as the "strig." This is bent at obtuse angles along its length and has four short branches at each angle. Each of these branches carries a seed or abortive ovary enclosed in a "bracteole," while two "stipular bracts" are attached to the strig immediately below each of the four bracteoles. Thus the cone consists of a series of bracteoles in fours enclosed by two bracts, the groups being situated on alternate sides of the strig, as shown in the partially dissected cone in Fig. 42. The bracts and bracteoles form what are commonly referred to as the "petals," but they are not part of the floral envelope and the word is here a misnomer. The bracteoles are oval-shaped and slightly incurved at the base to carry the seed. The bracts are coarser, somewhat larger and usually pointed at the tip. Very occasionally an ordinary green leaf grows within the cone from a point above a pair of bracts. The two bracts and four bracteoles of one group are shown in Fig. 43.

By the end of July or beginning of August, small cup-shaped bodies appear at the base of the bracts, around the seeds and on the lower surface of the bracteoles. These are the lupulin glands, which become filled with oily resinous matter. This is at first transparent and golden yellow in colour but, as the hops ripen, it becomes opaque, like flowers of sulphur, forming the pale yellow, powdery "condition" which is so easily shaken out of ripe hops. It is also known as lupulin and contains the largest proportion of the substances which are of use in brewing, the resins and oil which communicate the stickiness to the hands and give the aroma when cones are rubbed down. On drying, it again becomes transparent and golden yellow, but darkens in colour if the hops are dried at excessive temperatures. Fig. 44 is a photomicrograph of part of a bracteole of a dried hop cone covered with lupulin.

The seeds are of no brewing value and are, indeed, objectionable, since they may cause obstruction in the delivery main or pans of refrigerators or in cask taps and be detrimental to head retention on account of the oil they contain. In the majority of Continental countries the production of seed is prohibited, as it is held to impair the quality and flavour of the beer. Male plants are consequently rigorously excluded from gardens and their



FIG. 43
BRACTS AND BRACTEOLAS OF DRIED HOP CONE



FIG. 44
BASE OF BRACTEOLE OF DRIED HOP WITH LUPULIN

[Facing page 338]

neighbourhood. In England and America the growth of male plants is permitted and has a definite agricultural advantage, as fertilisation curtails the period in brush and thus diminishes the danger from mould. In addition, the hops grow out much better after fertilisation and the crop may be increased by several hundred-weights per acre. It was found by Salmon and Amos that well-seeded cones may be double the length of the same hops unfertilised.

This increase in weight is largely fictitious from the brewer's point of view, since 20 to 30 % of it may be due to useless seeds and strigs. The strigs of seedless hops are relatively small, but may account for between 5 and 10 % of the weight of the cone. They become longer and more prominent with increasing quantity of seeds and generally account for between 10 and 12 % and sometimes up to 15 % of the weight of English and American hops. The quantity of seeds in fertilised hops varies very considerably, from 7 to 10 % of the cone weight is quite normal and, not infrequently, from 15 to 20 % of that of English and American hops is due to seeds.

Seedless English hops are usually very small, largely on account of the smaller number of petals, 27 to 30 per cone, as compared with Continental varieties with 35 to 54 petals, which develop a comparatively large seedless hop. The reduced size and diminished crop seriously militate against the economic, but much to be desired, possibility of growing seedless hops in England until new varieties of good quality, better adapted to this form of cultivation, are introduced. Consequently it is the custom to grow one male plant to every 200 female plants in English and American gardens. These are planted on the windward side of the garden and so selected as to produce pollen at the time the female flowers are ready for fertilisation.

(253) Hop Growing.

The plant is perennial, producing fresh bine annually which may grow to a length of 25 to 30 feet, coiling clockwise round any available support. In the autumn the bine dies down, while the root stock and roots persist, penetrating deeply into the soil in the course of years. This manner of growth requires deep soil with good drainage, ample manurial treatment and a good deal of rain during the period of active growth in May and June. Different varieties are suited to different climatic conditions and soils. Thus a rather dry year in England is frequently referred to as a *Golding* season and a wetter one as a *Fuggle* season. Early frosts are not harmful but they may be disastrous in June or

July, as are hail storms. Shelter from wind is very important and is assured, if necessary, by plaited straw hangings on the windward side of the gardens. Rain in August and September is not desirable, as it may hinder picking and spoil an otherwise good crop, particularly if associated with a damp, warm atmosphere

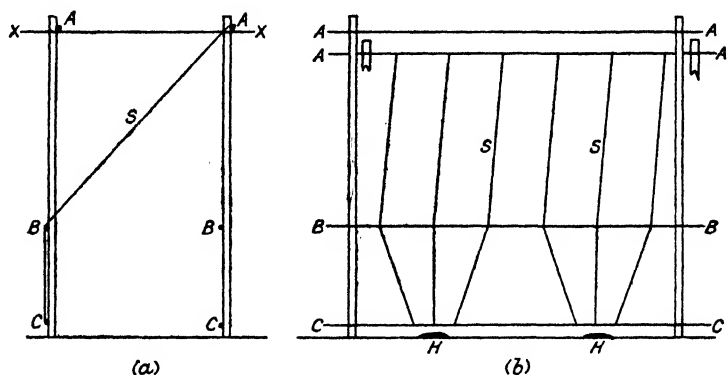


FIG. 45

BUTCHER SYSTEM OF TRAINING HOPS, END AND SIDE VIEWS
AA, Top wires; BB, Middle wires; CC, Bottom wires; XX, Cross strain wires
H, Hop hills; S, Strings

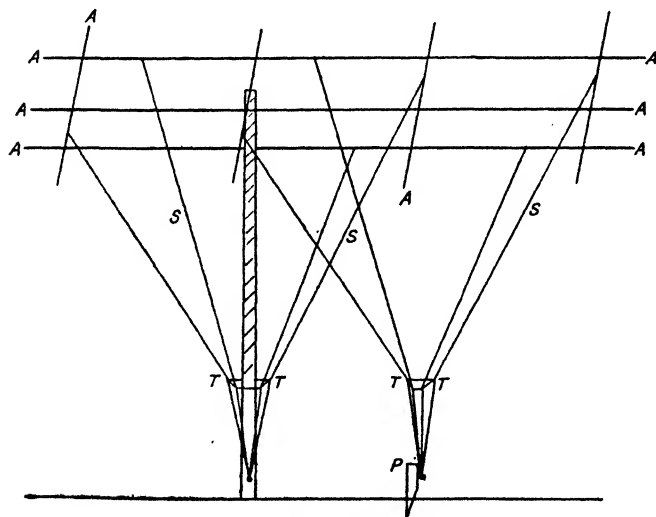


FIG. 46

THE UMBRELLA SYSTEM

AA, Top wires; S, Strings; TT, Coupling strings; P, Stump

during the day followed by cold nights, which favour the development of mould and Downy mildew. Intensive cultivation is required to improve the tilth and keep down weeds. It includes removal of what remains of the previous year's growth of bine, ploughing down, harrowing, rolling and, later, ploughing earth up to the hills.

Formerly the bine was trained up vertical poles but various systems of wirework carried on a reduced number of poles, usually 12 ft. 6 in. to 14 ft. high, or as much as 16 to 18 feet in the Worcester system, are now general. The hops are planted in hills 3 ft. 6 in. apart in rows 6 ft. 6 in. to 8 ft. wide in the different systems. The bine is trained and climbs up strings of coconut fibre attached to overhead wires. Brewers will be interested when visiting hop gardens in comparing the various pole and wirework

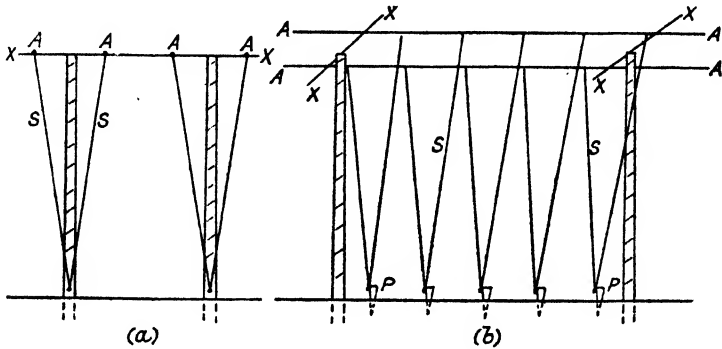


FIG. 47

THE WORCESTER SYSTEM

XX, Cross straining wires; AA, String wires; S, Strings; PP, Pegs

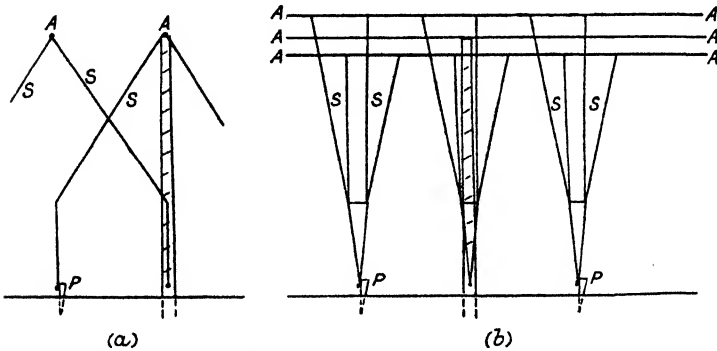


FIG. 48

THE CROSS BUTCHER SYSTEM

AA, String wires; SS, Strings; PP, Pegs

systems by which cultivation, spraying, washing and picking are facilitated, while exposing the growing bines to the full advantage of sun and air. Descriptions are to be found in the Ministry of Agriculture and Fisheries' pamphlet on the Cultivation, Diseases and Insect Pests of the Hop Crop,² from which Figs. 45 to 48 are reproduced. These represent the Butcher, the first system of wirework to be adopted in England, the Umbrella, Worcester and Cross Butcher systems. The last embodies advantages over the first

two, permitting unrestricted use of spraying and powdering machines, while the strains of the wires and strings are well balanced and the hops given good exposure to air and sunlight. Usually about 1,000 hills are planted to the acre but the Worcester system allows 50% more. It, however, only permits of lengthways cultivation, but the heads are carried over the centre of the alleys and are more easily washed than with the other systems.

(254) Ripeness of Hops.

As hops ripen, the cone becomes crisp to the touch and should contain plenty of lupulin. The bracteoles tend to a primrose yellow but the bracts remain greener and the seeds become purple. Maximum brewing value generally coincides with the period of growth at which the hops would be judged to be ripe by an experienced grower. The diagram in Fig. 49 by Walker and Hastings³

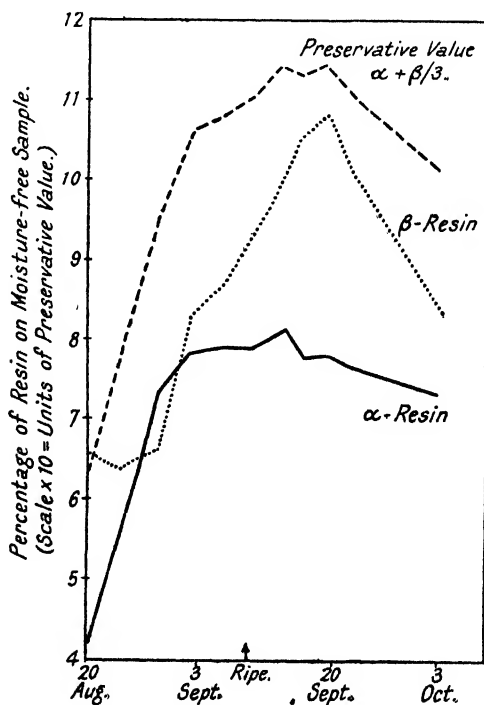


FIG. 49
CHANGES IN PERCENTAGES OF RESINS OF HOPS AT RIPENING

indicates a rapid increase in the α -resin content of a Canterbury Golding hop during the last fortnight in August, in this case followed by a period in which there was practically no alteration in this constituent of the resins, though the β -resin content still

continued to increase. The increase in β -resins went on for about eleven days after the hops were judged to be ripe. The significance of this change in the relative proportions of the resin fractions and its bearing on the brewing value of the green and fully ripe hops is explained later. The diagram illustrates the need to await full ripeness in order to secure the maximum resin content.

Changes in other important constituents go on concurrently with those in the resins. Development of the essential oils is of great importance, particularly for dry hopping purposes. It was found, when the hops were boiled with wort, that the most fragrant aroma was obtained about a week prior to the date on which the grower pronounced the hops to be ready for picking. The aroma began to deteriorate at the time picking commenced and had become decidedly coarser a week later. The percentage of tannin was found to be subject to much smaller changes, increasing in actual weight to an almost constant value at a rate relatively less than the rate of increase in the weight of the cones.

The period of maximum brewing value, as judged by analysis of the resins, varies with different hops, which are said to "hang" well or badly as the case may be. In the particular instance given it lasted ten days. The primrose colour of the hops changes to brown as they hang, a change which may be greatly accentuated by wind and weather and is sometimes difficult to distinguish from the damage caused by fungi. It adds some colour to the beer but, when this is of relatively small importance, the greater preservative value associated with maturity should recommend the slightly brown hops in place of the green and imperfectly ripe samples. The preference of some brewers for greener hops may be dictated by the aroma and suitability for delicately flavoured beers. Greater delicacy would preferably be obtained by selecting varieties characterised by this property.

The length of time through which hops will hang without serious deterioration is of considerable importance to both growers and brewers. It may be insufficient for picking a whole garden and the growers may consequently have to commence earlier than they would wish. There is almost bound to be a gradation of colour and ripeness in a large growth, possibly accompanied by a certain amount of weather or mould damage in later pockets. This temptation to early picking is greatly increased by the fear of Downy mildew or mould, which may ruin the crop of an entire garden if an opportunity of picking offered by good weather is missed.

Picking usually commences in England about the first week in September. The strings are cut down or unhooked at the top, after which the cones are picked off and loaded into bins or baskets.

Large machines for removing the hops from the bines are in some cases used, more particularly in America. The bines are frequently left on the ground until they wither, though they are destroyed as rapidly as possible if infected with Downy mildew.

(255) Hop Drying.

Hops cannot be used or stored in the green state and processes of drying are adopted not only to stabilise their active constituents but also to develop the most attractive flavour. Drying is still frequently carried out over open fires of anthracite, about 14 feet below the level of the drying floor of horsehair on which the hops are spread to a depth of about 10 inches. In more modern kilns the open fire is replaced by a closed stove or outside furnace. In such kilns, of which there are several types, the products of combustion do not come into contact with the hops, which are dried by a current of heated air. In some, the air is heated by passage of the hot gases through pipes radially disposed in the chamber below the drying floor. In others, the air is passed over a battery of steam pipes or through pipes in a furnace in an adjoining building and drawn by fan into the drying chamber. A return has been made to direct heat in some new kilns in which the furnace is replaced by oil jet burners, while similar jets are applied to closed furnaces with automatic control of the oil and air supplies. Ventilation was formerly secured by a cowl at the apex of a conical roof 16 to 20 ft. above the hops, but in newer oast houses a louvre roof is generally substituted, the air current being caused by fans above or below the hops. Some comparisons of hops dried over open fires and with pure air systems, by Burgess,⁴ showed little if any difference in the quality of the dried hops, the main object of pure air drying being to avoid contamination of the hops with impurities from the coal. Most of the information at present available on the influence of air speed and temperature on the rate of drying and quality of hops is to be found in A. H. Burgess' reports on investigations at the Institute of Brewing Experimental Oast.

The temperature of drying has a considerable influence on the quality of the product, the aroma and colour deteriorating as the temperature is increased. The preservative value of the hops also decreases with rising air temperatures. In Kent it is usual to commence drying at about 100° Fahr., rising to about 140° in the course of 8 hours and afterwards to about 160°. Some growers reduce all the temperatures by about 20°, but the ability to do this depends largely on the construction of the kiln. The time required to dry hops down to a moisture content of 7% depends

both on the temperature and air speed, so that reduction of temperature in any particular kiln extends the time of drying and may make it impossible to deal with two loads in 24 hours, as is usually necessary, the normal drying time being about 10 hours. Temperatures below 140° are consequently frequently impracticable and may in some cases be inadvisable.

Examples are given in Table 97 of the results obtained by Burgess⁵ at the Institute of Brewing Experimental Oast showing the effects of different drying temperatures on the soft resins. The figures show that the α -resin content becomes less as the temperature is increased but the percentage of β -resins is almost unaltered. Analyses of the same hops after 3 and 13 months' storage showed very little change in the β -resins but a considerable fall in the α -resin content. The temperatures are those registered by a thermometer below the hair. The hops themselves do not reach these temperatures. With air at 122° Fahr. they reach 118° in 2 hours and then remain constant. At 140° the hops attain 126° in about 90 minutes and then remain about 14° or 15° below the temperature of the air until dry. When drying with air at 158°, it was found that the temperature of the hops continued to rise throughout, reaching 140° or 142° when they were ready to remove from the kiln.

TABLE 97.—EFFECT OF DRYING TEMPERATURE ON RESINS OF HOPS
(PER CENT. RESINS ON DRY MATTER)

Hops	Air Temp.	Resins %			3 months			13 months		
		Resins %		$10\left(\alpha + \frac{\beta}{3}\right)$	Resins %		$10\left(\alpha + \frac{\beta}{3}\right)$	Resins %		$10\left(\alpha + \frac{\beta}{3}\right)$
		α	β		α	β		α	β	
A	122°	7.01	5.20	87.4	3.96	7.20	63.6	3.76	7.13	61.4
	140°	6.78	5.92	87.5	5.23	6.42	73.7	3.78	6.14	58.3
	158°	6.57	5.73	84.8	4.92	6.00	69.2	—	—	—
B	158°	5.05	4.82	66.6	4.72	5.05	64.0	4.03	4.82	56.4
	176°	4.91	5.35	66.9	4.47	5.15	61.9	3.82	4.46	53.1
	194°	5.12	4.70	66.9	4.30	5.90	62.7	3.56	5.76	54.8
	212°	4.60	5.48	64.3	3.93	5.42	57.4	3.50	5.47	53.2

By combining the results of a number of similar trials and thus eliminating unavoidable sampling errors, it was found that the relative preservative values of hops dried at different temperatures were as shown in Table 98. These are calculated from the gravimetric analyses and expressed in proportion with the average figure for hops dried at 158°, taken as 100.

TABLE 98.—DRYING TEMPERATURE AND PRESERVATIVE VALUE OF HOPS

Temperature Fahr.	Relative P.V.
104°	126
122°	117
140°	107
158°	100
176°	92
194°	88
212°	71

Although the appearance and consequently the market value of hops may be improved by drying at comparatively low temperatures, experimental brews have shown⁶ that the best results for ales are obtained with hops dried between 140° and 158° Fahr. Hops dried at lower temperatures were lacking in flavouring properties, while those dried at higher temperatures gave ranker flavours or had lost all hop character.

A dull appearance characterises hops which have been submitted to excessive heat while still moist. This may occur if the hops are allowed to remain in the poke and heat spontaneously before they are loaded to the kiln. Green hops contain between 60 and 80% of moisture according to their ripeness and the kiln draught must be sufficient to carry away the moisture without condensation in the upper layers of the hops, which otherwise become heated or "reeked." This seriously affects the appearance and flavour of the hops and is due to the fact that while 360 cubic feet of cold air can contain only 1 oz. of water, 4½ and 20 oz. can be carried without condensation by the same quantity of air at 100° and 150° Fahr. respectively. Air rising through the bed of hops gradually picks up more moisture but becomes cooler. Should this result in saturation, condensation may occur if the air is cooled at the top of the bed of hops. Consequently the drying temperature must only be allowed to rise slowly when the draught is poor. The highest temperature is not reached until the hops have "feathered," that is when the bracts have become almost dry and have opened like the feathers of a bird.

The air temperature is taken by a thermometer below the hair connected to a dial outside the kiln. Huber⁷ found that an air temperature of 175° was safe at the commencement of drying when the draught was good, under which conditions rapid evaporation kept the temperature of the hops down to 104° Fahr. The preservative value of the hops was found to be unaffected by an air temperature of 140° if the moisture was not reduced below 10%.

158° Fahr. was found to be permissible if the moisture of the hops did not fall below 12%. It was found that it was best gradually to reduce the air temperature to 104° Fahr. as the moisture was removed.

Sulphur dioxide, derived from burning sulphur, is passed through the hops during the early part of drying. This greatly improves the colour and aroma of the dried product and also appears to help preserve the hops when in cold storage. Without it hops develop an odour resembling dried leaves. Burgess⁸ found that the amount required was 1 oz. of SO₂ per every 1,000 cubic feet of air passed through the hops during the first hour of drying. The quantity of sulphur required consequently varies with the draught. Excessive quantities of SO₂ in hops are objected to, since the SO₂ content of the beer may be unduly raised and defective flavour may result. The purity of the sulphur has to be assured, as some samples are contaminated with arsenic.

Modern kilns are designed to minimise the breakage of cones and are generally fitted with roller hairs, on which the hops are carried forward and gently dropped on to the cooling floor. The hops are allowed to remain in a heap for from 4 to 8 hours or until their moisture content has risen from the 6 to 8%, to which they were dried, to about 10%, so that the cones become sufficiently tough to withstand packing. Insufficiently dried hops, containing up to about 16% of moisture, are sold as "cold packed" to be used rapidly, as they will not keep. Improved kilns, of which the Linhart is an example,⁹ are now constructed with several drying floors, the hops after partial drying on one are dropped to the next, where they meet air at a rather higher temperature.

In Germany and Czechoslovakia the hops are usually given only a preliminary drying by the growers, the process being completed by merchants. Air-heated kilns are used in Czechoslovakia but in the Hallertau, the largest German hop-growing district, open-fire kilns are generally used. In the other Bavarian and German districts, the preliminary treatment is still largely carried out by the old method. The hops are placed by the grower in sheds, where they are partially dried under the influence of air currents from windows on either side. After this preliminary drying, by whatever method it is carried out, the hops are more or less loosely packed in bales, according to their condition, and taken to merchants' warehouses, where the drying is completed and the hops are cured and packed. A small quantity of sulphur is used to destroy micro-organisms. The whole process is under official control in the case of certificated hops. There are, in addition, official packing houses in the hop-growing districts, where the packing can be done immediately after

delivery from the growers at fixed rates, but only a smaller proportion of the crop is dealt with in this way.

(256) Packing and Marking.

English hops are packed in cylindrical cloth pockets, which must be marked with the name of the grower, the parish, county, year of growth, serial number and gross weight. The pocket is attached to a collar beneath a circular opening in the floor of the cooling room and the hops are packed tightly into it by means of a screw press. When full the open end of the pocket is sewn up. These pockets are about 6 ft. in length and contain approximately $1\frac{1}{2}$ cwt. of hops. The Continental bales, packed in stouter cloth for export, contain about 3 cwt. In some cases the hops are compressed more heavily into 2 or 3 cwt. ballots and packed in metal-lined cases or iron cylinders.

American hops are packed in a manner which is more economical for transport and storage. The baling press is of box type with removable ends. The box is filled with hops which are rammed down. Another lot of hops is introduced, covered with the top cloth and rammed again. The cloths are finally sewn together at the ends and sides of the rectangular bales. As the open top of the box forms one of the sides of the bale and not a top, as in an English pocket, the grain of the packed hops is lengthways instead of across the pocket. Comparatively light cloths are used, as they do not take the pressure of packing. The bales contain about 200 lb. of hops.

A strict system of marking Saaz hops, accompanied by a seal and certificate, has been a feature of the Bohemian hop market for many years. This became compulsory for all Czechoslovakian hops after passage of laws in 1921 and 1922 which enacted that all hops should be marked with the district and year of production. The certification and sealing is undertaken by an official Marking Hall in each district, under authority of the Ministries of Agriculture and Commerce. All hops are inspected by an official before they are packed and he issues a certificate of weight and seals the bales, which are numbered and cannot be repacked without authority of the Marking Hall. Germany adopted a similar system in 1929, since when all bales must bear the words *Deutscher Siegelhopfen* and be certified, with the name of the State, place and year of growth, sealing authority and a statement whether they have been opened or not. This method of marking hops in countries where the varieties grown are few and can be indicated satisfactorily by the name of the district, coupled with an official system of examination, amounts in practice to a guar-

antee that the quality of the hops does not fall below an equitably fixed standard for the year. Its advantages have proved so great that Poland has taken steps to adopt a similar plan.

(257) Storage of Hops.

Though hop drying destroys both humulon and lupulon to a certain extent and reduces the preservative value of hops by half or three-quarters, it stabilises the composition of the resins and prevents further rapid resinification of the humulon and lupulon during storage, possibly largely by destroying some of the micro-organisms which would accelerate it. Nevertheless hops are subject to deterioration in flavour and preservative value during storage, through oxidation of the oil and resins and on account of the action of micro-organisms in the presence of moisture. Few hops of the current season are used before Christmas, except for the few pockets which have been dealt with as cold packed. During the succeeding months the new hops are used in gradually increasing proportion with others carried over from the previous season. Careful storage is consequently necessary to preserve the hops to the best advantage throughout the period in which they will be used. The growth of micro-organisms and the activity of enzymes are restricted but not prevented by storage at 32° Fahr. in a fairly dry atmosphere. In consequence a large proportion of the crop is placed in cold storage in December or January and all should be in before March at latest. The most satisfactory cold stores are those in which the temperature can be maintained at 32° to 33° Fahr. by means of a restricted current of air, with a relative humidity of 75%.

Two typical analyses of Kent Fuggle hops, ¹⁶ showing the nature of the changes in the resins during storage, are given in Table 99.

TABLE 99.—ANALYSES OF HOPS DURING STORAGE
(PERCENTAGES ON DRY HOPS)

Storage period	Cold store			Warehouse		
	<i>α</i> -resin	<i>β</i> -resin	P.V.	<i>α</i> -resin	<i>β</i> -resin	P.V.
5 months	6.28	8.60	91.5	6.67	9.26	97.6
9 months	6.22	8.20	89.5	5.83	9.17	88.8
14 months	5.72	8.25	84.7	4.72	9.34	78.5
19 months	5.84	8.54	86.9	3.48	8.64	63.6
19 months	5.15	8.92	81.2	2.21	9.90	55.1

They represent two pockets of the same growth kept in warehouse and cold store and show the advantage of low temperature storage, which may slow up the action of micro-organisms very materially.

The marked fall in α -resin with very small change in β -resin during the first 18 months will be noted. After this the β -resin apparently increased. The first analyses were made when the hops were placed in cold store in November.

The analyses in Table 100 of three different Kent Fuggle hops, two, three and four years old, show the almost complete loss of α -resin in old hops. It is explained in the next chapter that the preservative value of hops depends on constituents of the soft resins which can be divided by analysis into α - and β -fractions, referred to as α -resin and β -resin in the present Tables. The former consists of an acidic substance, known as Humulon. This is gradually converted during storage to products of lower antiseptic potency included in the β -resins. At the same time, the most active constituent of the original β -resins, known as Lupulon, is rather rapidly resinified and the percentage of hard or γ -resins, with no preservative properties, increases. These changes are correlated with reduction in the preservative value of the hops. The advantages of cold storage include a considerable slowing up of these processes of resinification, as well as a marked retardation in the physical deterioration of the hops. The analyses in Table 100 probably under-estimate the quantity of humulon (see Section 274) and consequently the preservative value of the hops. Tests with bacteria in biological analyses show relatively higher preservative properties with old hops, and brewing experience indicates that they have a better value, from this point of view, than the gravimetric analyses suggest. Biological analyses show a comparatively rapid fall in preservative value during the earlier stages of storage, which is possibly associated with the decomposition of lupulon.

TABLE 100.—ANALYSES OF OLD HOPS

Age	per cent. on dry hops			P.V. 10 $\left(\alpha + \frac{\beta}{3}\right)$
	α -resin	β -resin	γ -resin	
2 years ..	2.23	6.80	4.07	45.0
3 „ ..	0.56	7.68	5.36	31.2
4 „ ..	0.18	7.57	5.85	27.0

The two analyses of lupulin in Table 101 do not represent the same sample, though they would probably have been very similar when fresh. They clearly show the change in humulon or α -resin and the accompanying great increase in hard resins. It is not known to what extent the small change in the β -resins is due, if at all, to a balance between changes from α - to β - and from β - to

hard resins. These changes in the resins are accompanied by loss of bitterness, which is largely due to the humulon in new hops. The hard resins have comparatively little flavour, but its character is rather unpleasant.

TABLE 101.—ANALYSES OF LUPULIN FROM CALIFORNIAN HOPS

					6 months old	4-5 years old
Soft resin	{	α -resin %	20.72	1.53
		β -resin %	30.88	25.45
Hard resin		%	17.30	46.90
					68.90	73.88

The action of oxygen on the aromatic and preservative constituents of hops may be reduced by storage in hermetically sealed metal containers or by extra compression of the pockets down to one-third or one-half of their original volume. Compression is carried out by hydraulic presses, without removal of the cloths. Circles of wood are placed at the top and bottom of the pocket previous to compression and, afterwards, the whole is bound with iron straps. Some brewers report success with this process and have been able to dispense with refrigerated storage, but the results are not always satisfactory. In any case the space required for storage is much reduced, a great advantage, provided the strength of the warehouse walls and floors is sufficient to bear the extra weight, and transport is facilitated. Little if any damage is done to the cones by extra compression, but most brewers prefer to reserve selected, uncompressed pockets for dry hopping.

The extent of the depreciation in preservative power of hops stored in ordinary warehouse and cold store is shown diagrammatically in Fig. 50, where the improvement resulting from extra compression in a particular case is also indicated (Walker, Hastings and Aldous¹⁰). CS 1 represents normally packed hops in cold store, CS 4 hops from the same growth compressed until the length of the pockets was reduced to 3ft. 11in. WH 1 and WH 4 refer to pockets of the same hops stored in an ordinary warehouse, WH 4 being compressed. It will be noticed that after 18 months' storage the hops in cold store had lost less than one quarter of their original preservative value, while those in the ordinary warehouse had depreciated to the extent of about one-third and that extra compression had been as effective in the warehouse as cold storage without compression. The quality of the hops in

these two pockets, as judged by physical examination, was found to be equal. Other trials on similar lines have shown that extra compression was of advantage for the first six or nine months in warehouse, but that little difference was produced in cold store and, occasionally, the compressed hops did not keep quite so well as in normal pockets.¹⁶

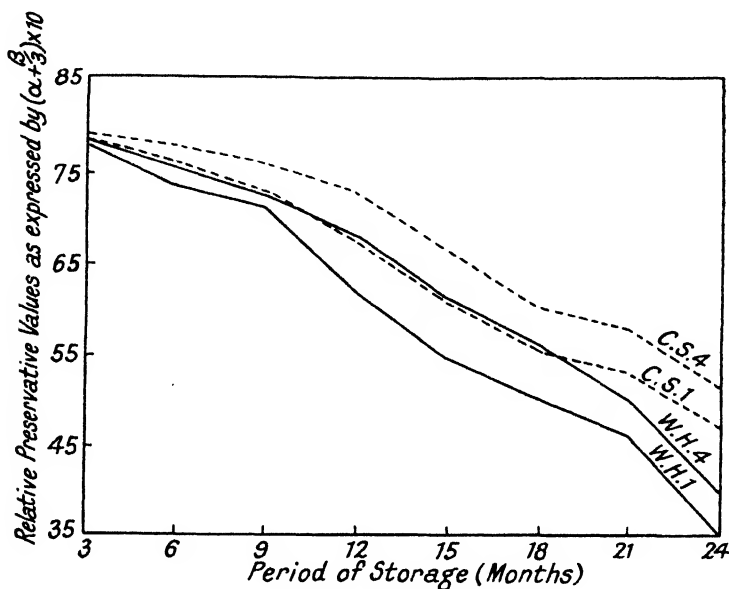


FIG. 50
CHANGES IN THE RESINS OF HOPS DURING STORAGE

According to Burgess,¹¹ the part played by micro-organisms in the deterioration of hops has hitherto been under-rated, while the influence of oxygen and enzymes has been stressed too much. He found that, although storage in oxygen appeared to accelerate the decrease in humulon content, this can still proceed in atmospheres of carbon dioxide or nitrogen. The deterioration of heat-sterilised hops was, however, only slight. This might be attributed to the destruction of enzymes, but experiments in which these were destroyed by steam previously to drying on the kiln indicated that enzyme destruction did not prevent deterioration. This left the possibility that micro-organisms, which subsequently gained access to the hops, were the chief cause of their deterioration, a point which remains to be settled by determination of the effects of various bacteria and moulds isolated from deteriorating hops. Positive results have already been obtained with *Mucor spinosus*, *Penicillium expansum* and *Aspergillus niger*.

DISEASES AND INSECT PESTS OF THE HOP

(258) Fungoid and Virus Diseases.

The high cost of hop growing entailed in the elaborate systems of pole and wirework and careful cultivation is greatly increased by the continuous labour required to combat diseases and insect pests by spraying and washing. Salmon¹² listed eleven fungus and ten virus or supposed virus diseases of the hop but others are liable to be added as they spread to the hop from other plants or are newly identified. The two commonest fungus diseases are Downy Mildew and Hop Mould, the most dangerous virus diseases being Nettlehead and Mosaic. The damage done in some cases is so extensive as to destroy the entire crop of a garden, while in others the bine is so weakened and the cones deformed or discoloured to such an extent that their brewing value is seriously diminished. The brewer is thus affected both by reduction of crop and by the production of inferior hops. When the damage to the cones is not very extensive it is often difficult to distinguish from the discoloration due to wind or the brown of very ripe hops.

(259) Downy Mildew (*Pseudoperonospora humuli*).

This is at present the most dreaded of hop diseases and few districts are free from its ravages. It was observed in Japan in 1905, and in America in 1909, but was unknown in Europe until 1920, when it was detected at Wye and studied by Salmon and Ware,¹³ from whose publications the particulars and illustrations given are taken. It is a wet weather disease caused by a fungus which produces two kinds of spores, *conidia* or summer spores, which occur in dense greyish-black masses on the leaves, stems and cones, and resistant winter spores. The latter are round, thick-walled cells produced inside the leaf, stem or shoot. These are probably set free when the plant decays in the autumn and, after spending the winter in the ground, germinate and infect the plant in the spring or summer.

The branched structure of the fructification, Fig. 51, is very distinctive and can be readily identified by means of a pocket lens. When the summer spores are ripe they fall off and, if they reach a moist spot, may each produce 4 to 7 or more swimming spores or *zoospores*. Any of these settling on a leaf or cone will penetrate the tissues and produce a mycelium, from which branched growths and spores may develop in a week. Cones approaching ripeness may suddenly be attacked in wet weather and spread of the disease is so rapid that whole gardens may become brown in two or three

days. The bracteoles are more readily attacked than the bracts and, turning brown first, give the cones the appearance shown in Fig. 53.

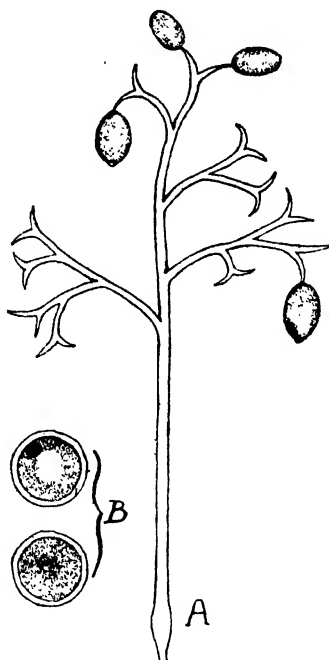


FIG. 51

DOWNY MILDEW, (A) BRANCHED FRUCTIFICATION BEARING SUMMER SPORES $\times 250$
(B) TWO RESTING SPORES TAKEN FROM AN INFECTED LEAF $\times 250$

The first evidence of attack by Downy mildew is the appearance in March or April of stunted "basal spikes," Fig. 52, among the young healthy bines. The spikes must be destroyed as soon as they appear to prevent spread of the disease by the black masses of spores which form on the underside of their curled leaves. The pith of the spikes is turned brown by the invading mycelium. The production of pale yellow spots which in a few days become brown and angular is characteristic of attacked leaves, Fig. 53. Lateral or terminal spikes may also form on growing bines. Spread of the fungus from leaves and spikes to the burr in suitable weather may cause very serious loss, as the burr is destroyed and becomes greyish-black in colour.

Protective measures include scrupulous removal of all spikes and spraying three times, or four times in wet seasons, with Bordeaux mixture or cotton seed oil-copper sulphate emulsion. The former contains 10 lb. of copper sulphate and 15 lb. of hydrated lime in 100 gallons of water, the latter 5 lb. of copper sulphate, $7\frac{1}{2}$ lb. of hydrated lime and 6 pints of cotton seed oil in 100 gallons of



FIG. 52

DOWNY MILDEW, YOUNG HEALTHY VINE AND, ON RIGHT, INFECTED BASAL SPIKE
(ABOUT $\frac{2}{3}$ NATURAL SIZE)

(Facing page 354)



FIG. 53

DOWNY MILDEW ON CONES AND LEAVES OF HOP (COBB)
(ABOUT $\frac{1}{2}$ NATURAL SIZE)

water, to which nicotine may be added if it is desired to kill aphids at the same time. The four sprayings are carried out (1) when the majority of the bines have reached the top wire, (2) when the pin is just beginning to show, (3) when the burr is beginning to appear and (4) immediately the burr has disappeared. If this procedure is adhered to the cones should be practically free from copper at picking, but in many cases 100 to 200 parts per million of copper are found on the cones, but little of this is imparted to the wort.

Little damage may be done to the brewing value of the hops when the attack is slight and the hops nearly ripe, as the lupulin glands are not affected. In such cases it may be difficult to detect the fungus, since the colour of the cones is improved by drying, but destruction and decay will be noted in the packed hops after earlier and more serious infections. The susceptibility of different varieties of hops to Downy mildew varies and for some years the cones of the Fuggle resisted so well as to suggest immunity but this hop ultimately succumbed, though it is not so susceptible as Goldings and Golding varieties and one spraying less may be adequate to protect it.

(260) Hop Mould.

This fungus (*Sphærotheca humuli*) can readily be distinguished from Downy mildew by the structure of the fructification, Fig. 54. The mycelium of fine white or brown *hyphæ* forms masses of threads over the attacked surface and sends down branches or suckers into the tissues of the leaf or hop, extracting nutriment from the sap and destroying the vitality of the plant. Upright branches, known as *conidiophores*, bearing a necklace-like chain of *conidia* or summer spores, also arise from the mycelium and form the fructification. The spores separate from the chain when they ripen, accumulating in white powdery masses, which may be blown to other plants and cause a rapid spread of infection in favourable weather. The spores germinate and send suckers down into the new host within 24 hours and a powdery patch of mould with summer spores is formed in a week or ten days. Later in the summer, minute round blackish-brown conceptacles or *peritheciæ* may be found under the hop leaves or on mouldy cones. Each of these contains a transparent sac or *ascus*, holding eight winter spores or *ascospores*, which, in their resistant covering, gain access to the ground from mouldy hops which have been left unpicked and not destroyed. In this form they pass the winter.

The two different stages of growth have given rise to the names Red and White mould, which actually refer to stages in the life

history of the same fungus. Usually about May the conceptacles open and liberate the winter spores, which are carried by the wind to the growing plant and rapidly develop into patches of white mould. Methods of prevention include powdering with flowers of sulphur to smother white mould. Repeated applications are given throughout the season with knapsack or mechanical blowers to prevent the spread or destroy any red mould that may appear. Solutions of liver of sulphur and of soft soap are also sprayed over the hops, particularly in damp weather when the powder would be washed off. Colloidal sulphur is also used with the washes employed to destroy aphids.

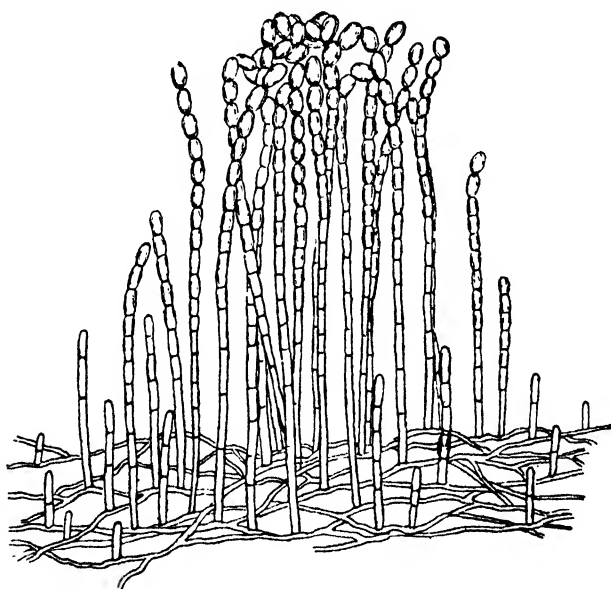


FIG. 54
FRUCTIFICATION OF HOP MOULD

Mould causes the greatest damage when it attacks the burr, particularly when in brush. Each flower may be turned into a hard white knob, so that no hops develop and there is no hope of saving a crop badly damaged at this stage. Hence the advantage of male hops to hasten the development into hop and the necessity to apply sulphur at an early stage. When cones are attacked they become partly or entirely destroyed. The hop may be covered with white mould or eaten into at one side. Ripe hops are usually attacked by the winter spores and become foxy red in colour, an appearance that is not always easy to distinguish from weather damage in packed hops.

(261) Other Fungus Diseases.

The term "wilt" is applied to fungus diseases in which the mycelium invades the water-conducting parts of the plant and, by cutting off the water supply, causes the leaves and stems to wither and die. Three diseases of this kind attack the hop plants, of which Hop Canker has been longest known. It is believed to be caused by a *Fusarium* and may cause great damage through wilting the bines and canker of the root-stocks. Two other wilts are caused by *Verticillium albo-atrum* and *Sclerotinia sclerotiorum*. Other fungoid diseases recorded by Salmon are Leaf-spot (*Cercospora centuariensis*), Die back (*Phoma* sp.), attacking the upper part of the bine, which dies back, Grey mould (*Botrytis cinerea*) and Black mould (*Cladosporium* sp.) which may cause brown discoloration of the outside of the petals during picking in wet weather, Hop drop, causing the cones to fall to the ground and Honey Fungus. These are of comparatively small importance.

(262) Virus Diseases.

These diseases differ from those already described in that their incidence cannot be traced to development of a fungus. They are generally attributed to occurrence in the sap of a virus or ultra-microscopic organism which is communicable from plant to plant by insects, particularly aphides. A more recent suggestion¹⁴ is that the virus may be a colloidal, high molecular, enzymic protein of specific constitution which, on transmission to a plant, may be supposed to lead by catalysis to the transformation of gel proteins into active enzymic proteins in a sol condition, with consequent physiological effects. The most destructive hop diseases of this type are Nettlehead and Mosaic disease. *Nettlehead* or *Eelworm disease* chiefly affects the Fuggle variety, weakens the bine and causes it to fall away from its supports, the leaves becoming curved inwardly at the edges and pale in colour, while affected hills are barren or produce only a few worthless cones. It slowly spreads through a garden and the only remedy appears to be grubbing up. Its second name arose through earlier attribution to the eelworm, which is frequently found at the roots of infected hops. Several of the new varieties produced at Wye College appear to be immune from this disease and should be useful for replanting. Among these are Brewer's Favourite, Fillpocket and Quality Hop.

Mosaic is much more destructive than Nettlehead and is noted through cessation of growth of the bines and curled leaves with mottled green and yellow colour. The bines remain barren. The Golding hops and Golding varieties are the most susceptible. Fuggle's, which is attacked by Nettlehead, is immune, as are

Colegate, Tolhurst and a number of the new varieties. A striking feature of this disease is that all immune varieties are carriers and may, if infected, cause the spread of Mosaic to adjacent susceptible hops. Affected hills are immediately grubbed up. Carrier varieties should be planted in isolated gardens or adjacent to Fuggle's but not to such susceptible hops as Goldings. Affected plants produce no crop in the second year and are killed either that year or the next. None recover and the disease spreads very rapidly in the rows unless the affected hills are removed.

Chlorotic disease is a rarer virus disease in which the leaves show conspicuous yellow markings, accompanied by distortion. "Fluffy-tip" or "Bunchy-top" is probably also caused by a virus and was given its name on account of the fluffy or feathery appearance given to the tips of the bines. "Split-leaf," "Split-leaf Mottle," "Small Hop" and "Crown Gall" are other diseases occasionally met with, of which the causes are unknown.

(263) Hop Aphis.

The three most destructive insects are the Hop aphis, the Red Spider and the Wireworm, which is the larval form of the Click or Skip Jack beetle (Jary¹⁵).

The Hop aphis (*Phorodon humuli*) passes the winter in the egg stage on sloe, damson, bullace and plum trees and is consequently also known as the Hop-damson aphis. The first insects to hatch from the eggs in the spring develop into females, which produce young viviparously. These reproduce in the same manner until, in May, some green winged migrants appear and fly to the hops, where they are known as the fly, and rapidly produce living wingless young or "lice," but no eggs. Breeding may be very rapid during damp weather, but is slower in dry, hot weather. In September and October winged females again appear and fly back to their winter homes, where they are followed by a flight of winged males.

The appearance of the "fly" is anxiously watched for in the spring, since it will, if not immediately countered, give rise to such an abundant development of "lice" or "black blight" that the undersides of the leaves will be covered. The aphides feed by sucking sap from the leaves and young shoots, thereby causing destruction of the leaves or weakening of the plants. It is believed, but not proved, that some of the virus diseases of the hops may be transmitted by the aphides when they pierce the plant. They are known to carry virus diseases in the potato. The aphides also cause damage by excretion of a sugary liquid "honey dew" on which mould develops readily and interferes with the normal breathing of the plant. If a late blight infests the cones the dead

bodies become infected with a fungus and the dried hops show a black core which destroys their value.

Aphides are combated with sprays of soft soap, quassia and nicotine or dusts containing nicotine as the toxic agent. This acts as a contact poison and kills soft-bodied insects by contact only. Hence large amounts of spray at high pressure are used completely to cover the foliage and wet the insects, for which reason the soap is added as a spreader.

(264) Red Spider (*Tetranychus altheae*).

This is not a spider but a mite or *acar*us, which in dry, hot summers may cause serious damage by sucking and gnawing the underside of leaves. It spins a fine silken web, which prevents the normal leaf respiration and, together with the actual damage done by the mite, kills the leaves and gives "fire blight." The mites are only about 0.5 mm. long but they can be very destructive on account of their numbers. Rain or moisture in the atmosphere kills them. Brick red females hibernate during the winter in the soil, in hedge bottoms, in cracks on the poles and elsewhere. About the end of April they crawl on to the plants and lay eggs in a small web on the underside of the leaves. These hatch out in a week or two and themselves lay more eggs in two or three weeks, which develop into yellowish-green mites in great numbers by July and seriously weaken the bine.

Their control includes use of a tar oil wash or carbolineum in the cracks on poles. Sprays of 1% lime sulphur are used to kill the red spider but nicotine does not kill them. Lime sulphur must not be allowed to come in contact with the cones, which it blackens. It also reacts with the copper in Bordeaux mixture, giving a black sulphide.

Other insects, such as the Flea beetle (*Plectrocelis concinna*) and the so-called "Cone flea" (*Psylliodes attenuata*), are of more local occurrence but may cause a considerable amount of damage unless controlled by means of Derris, for example. The caterpillars of the Sword grass moths, *Calacampa vetusta* and *C. exoleta*, can also bring havoc among the growing bines.

(265) Summary.

The hop is dicæcious, with male and female flowers on different plants, fertilisation of the female flowers being effected by wind-blown pollen from male flowers. The seeds produced are objectionable in brewing and male plants are not permitted in or near the gardens of most Continental countries. The cones of English hops, however, grow out much better after pollination. They also develop more rapidly, so that pollination tends to preserve the

cone from damage by mould at a time when it is very easily infected and may be entirely destroyed if attacked. The chief substances of brewing value, resins and oils, are produced in a resinous exudation in glands which, after drying, form the flour or lupulin.

The aim of the various systems of pole and wirework on which the bines are trained is to expose them to air and light, at the same time protecting the cones from damage by wind and permitting ready access for cultivation and spraying with the washes and powders required for protection against fungoid and insect pests. The chief fungoid diseases are caused by Downy mildew and Hop mould, which may destroy a garden very rapidly. The virus diseases Mosaic and Nettlehead are also very destructive. The most common insect pests are Hop aphid and Red spider.

Drying is still frequently carried out over open fires but in most modern kilns the hops are dried by air heated in some type of furnace and drawn through the hops by fans. The appearance and brewing value of hops are materially influenced by kiln treatment and drying temperature. The best flavour appears to be given to beer by hops dried between 140° and 158° Fahr., air temperature. Insufficiently dried hops are known as "cold packed" and those on which moisture has condensed on the kiln with damage to their flavour are known as reeked. Current season's hops are not used until after Christmas and the advantage of cold storage for hops to be used later in the year is considerable.

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CHAPTER XVI

THE USEFUL CONSTITUENTS OF HOPS

THE RESINS

(266) Constituents of Hops.

The figures in Table 102 are representative of the very varied composition of kiln-dried hops. Samples containing a higher percentage of moisture than 13 or 14 would generally be classed as "cold packed" and would deteriorate rather rapidly on storage. The slight diastatic activity is of importance in dry hops, as it assists in the slow breakdown and fermentation of dextrins in cask. Wild yeasts are occasionally present and may lead to frets or disturbances of a detrimental character. Only about 5% of moisture is found by drying hops *in vacuo* at 35° C.

TABLE 102.—CONSTITUENTS OF KILN-DRIED HOPS

	Per cent.
Moisture	9-13
Resins	10-20
Oil	0.2-0.5
Tannin	2-5
Pectins	9-11
Ash	6-10
{ of which P_2O_5	about 18%
K_2O	about 30%
Nitrogen	2-4
Glucose, fructose	2-4
Diastase	slight activity

Successive extraction in methyl alcohol and ether, cold water and hot water yields fractions in the following approximate proportions as percentages on dry matter (Fink¹).

TABLE 103.—FRACTIONATION OF HOPS BY EXTRACTION

Extracted by	Fractions	Per cent. on dry matter
Methyl alcohol and ether ..	Resins, oils, wax, etc. ..	33
Cold water	Sugar, tannin, nitrogenous substances, salts, etc. ..	12
Boiling water	Hydrated pectin	12
Residue	Pectin-free plant material ..	43

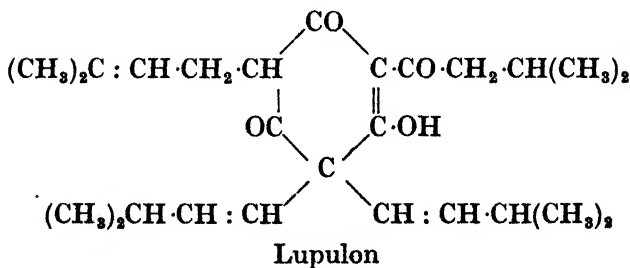
(267) Antiseptic Properties of Hops.

Practical experience has established the fact that hops function as a preservative in beer and comparative brews with hops of varying quality or variety² show that some are deficient in this most important property and that beers in which they are used rapidly become unsound, while others restrict the development of bacteria to a greater or less extent. On the other hand, Shimwell³ has shown that bacteria exhibit very varied degrees of resistance to the antiseptic action of hops. He found that very few Gram-positive bacteria grew at all in hopped wort and many, notably species of *Streptococcus*, *Micrococcus* and *Lactobacillus*, which thrive in sweet wort media might become dangerous in beer, were it not for the presence of hop extractives. *Lactobacillus pastorianus*, formerly known as *Saccharobacillus* and one of the least sensitive Gram-positive bacteria, was, however, less influenced by hops than was formerly believed.⁴ This organism and some *micrococci* or *streptococci*, which are Gram-positive or variable and sensitive to hops, are the commonest causes of biological defects in beer and the usefulness of hop antiseptics is greatest with them. The antiseptic effect is probably largely due to lengthening of the initial lag phase of bacterial growth. Gram-negative bacteria, such as *F. proteus*, the common rod bacterium found in pitching yeast, *A. capsulatum* and *A. viscosum*, which cause ropiness, are very hop tolerant, in contrast to the Gram-positive bacteria, while ropiness due to forms of *Micrococcus* frequently occurs in highly hopped beers.

The preservative or antiseptic properties and characteristic bitter flavour of hops are due to constituents of the resinous substances secreted by the lupulin glands during development of the cones. The general conception of a resin is a translucent, yellow or brown plant exudation, which has hardened on exposure to air into a non-crystalline mass with a vitreous appearance. The best known substances of this nature are derived from coniferous trees and are either inodorous or smell slightly of turpentine, but others have a characteristic odour from admixture of essential oils. They are generally mixtures of acidic substances, known as resin acids, closely related to the terpenes of which they are oxidation products. They are insoluble in water but mainly soluble in alcohol and ether. It is not known how closely the oily, sticky substance left on the hands after rubbing down hops is related to a typical resin in chemical composition, but it is allied in general properties and is referred to as hop resin. It is of variable composition and, after separation from the essential oils, contains a small quantity of fat or wax, mucilaginous material and a residue from the oils retaining their characteristic aroma.

Hayduck⁵ separated the resin which he had extracted from hops into two bitter fractions, the α - and β -resins, and a third, the γ -resin, of no antiseptic value. These can all be extracted from ground hops or lupulin, together with some wax-like material, by means of ether but only the first two are soluble in light petroleum spirit. These are known as soft resins, while the γ -resin is referred to as hard resin. From the first two fractions Hayduck isolated acidic compounds, which were called hop bitter acids. Bungener⁶ separated a crystalline acid from lupulin, which he called lupulinic acid and which was later shown to be the β -bitter acid. Bungener and Lintner⁷ isolated the α -bitter acid from the α -fraction. These acids are now known as Humulon, from the α -fraction, and Lupulon, from the β -fraction. They are not known to occur in any other plant product and are regarded as the original antiseptic and bitter substances in hops, giving rise to less powerfully and non-antiseptic resins, apparently by oxidation, polymerisation or hydrolysis. Humulon and lupulon give yellow and colourless crystals respectively and both are weak acids, humulon being the stronger.

Humulon and lupulon may be supposed to be synthesised during the growth of hops, the change to resins progressing during ripening, drying and storage. Wieland⁸ and Wöllmer⁹ have suggested that they may be represented by the following formulæ, respectively:



(269) Properties of the Resins.

A concrete idea of the nature of the resin constituents, so far as it is at present known, and of their properties is most readily obtained by study of the various methods of analysis which have been developed since it was realised that the antiseptic power of hops was associated with the resins and not with the essential oils or tannin, to which preservative properties had previously been attributed. Chemical and biological methods are both used in hop analysis.

The four chemical methods illustrate the varying solubility of the resin fractions in different liquids, together with the properties of the two acids which have been isolated from them. They show how the resins may be fractionated and give the first steps in the preparation of the acids, emphasising their acidic properties by titration methods and salt formation. Some striking reactions are also introduced in a colorimetric method of analysis and, taken together, they reveal the antiseptic substances as concrete entities. The biological methods provide a valuable introduction to biological technique, affording instruction in the preparation of pure cultures and their use. Since these methods are intended to determine the preservative value of hops, they must ultimately be compared with the results of biological processes of examination, devised to estimate the inhibiting or restricting influence of hop extracts or of solutions of the various fractions of the resins on the growth of micro-organisms, in accordance with the principles adopted in the assay of other antiseptic substances.

The colloidal character of the resins necessarily plays an important part in their behaviour during brewing. These properties, associated with complex particles and molecules of high molecular weight, are shared by humulon and lupulon and influence their behaviour when hops are boiled in the copper. Part of the humulon and lupulon is dissolved or dispersed in the wort, but part is adsorbed on wort proteins and precipitated as these are coagulated. Some of the dispersed humulon is then converted during boiling to α -soft resin, which has a lower antiseptic value than the original acid. (Section 278.) As a result of these changes a large proportion of the antiseptic activity of the hops is destroyed, the loss amounting to some 75% in experiments with pure humulon. The preservative value of the lupulon and associated resins is also greatly diminished during boiling. The changes in flavour produced during boiling are equally important in brewing and are influenced by the effects of salts in the wort, particularly gypsum and carbonates from the liquor. The behaviour of the resins during boiling are more fully dealt with in the sections on wort composition in Vol. II.

(270) Biological Methods of Analysis.

Adrian, Brown and Ward¹⁰ isolated a bacterium from acid beer which was morphologically very similar to *Lactobacillus pastorianus* but proved very sensitive to the presence of hops or their extracts and, in their absence, multiplied very rapidly in wort, producing lactic acid. It was named *Bacterium X* and used for comparing the antiseptic properties of hops. Brown and Clubb¹¹ employed for this purpose a 1.0% infusion of the hops in boiling water. This assumed that the toxic substances were soluble in water and were not destroyed or affected in such a way by boiling that the value of the method was diminished. The authors showed that the toxic substances went into true solution and that the essential oils did not contribute to the antiseptic action of hops. They emphasised the very important point that hop antiseptics do not kill the bacteria but merely slow down their initial development, that is lengthen the lag phase of growth, and found that the substances concerned were immensely more powerful than other well-known antiseptics. On the basis that 25% of the solid matter of hops is soluble in boiling water and assuming that this represents antiseptic substance, a very great over-statement, the authors concluded that hop antiseptics were 41.7 times as strong as phenol, 3.3 times as strong as potassium metabisulphite and only exceeded in lethal action on the particular bacterium used by mercuric chloride. Another point made was that only 0.18% of soft resins was found in an aqueous infusion of a hop that originally contained 13.3% of soft resins and yet this infusion had apparently $\frac{1}{4}$ of the toxic power of the original hops.

The conclusion drawn from this pioneer work on the biological assay of hops was that their toxic power was not proportional to the quantity of soft resins and must be due to some constituents that might vary in quantity, apparently the α - and β -acids, preparations of which were found to possess marked antiseptic properties. The final stage of the analysis depended essentially on measurement of the lag phase produced by addition of hop extracts to a culture of *Bacterium X*.

Ten ml. of bright cold water extract of malt was measured into each of a series of test-tubes. To each of these, known amounts of the hop extract were added and the tubes sterilised. After cooling, each tube was inoculated with one drop of a culture of *Bacterium X* and incubated at 80° Fahr. The cultures were examined from time to time to note when any of them became cloudy through bacterial development. That tube in which obvious growth was just prevented in 48 hours was taken as a measure of the inhibiting value of the hop infusion, and the relative antiseptic values of hops were expressed by the figure obtained by multiplying the

volume of infusion required to prevent growth in 48 hours by 200. Thus if 0.5 ml. was required, a value of 100 was assigned to the hops.

A drawback in this and other methods depending on the use of an aqueous hop decoction arises from the difficulty of obtaining representative decoctions, on account of the restricted solubility of the antiseptic substances and their alteration during the infusion at 212° Fahr. Ford pointed out that these could not be obtained at a higher concentration than 0.25%. The proportionality between the antiseptic potencies at increasing concentrations is definitely broken at 0.5%. Chapman noticed this difficulty in connection with the method just described but decided on 0.5% as a compromise to avoid the experimental errors involved in more dilute decoctions.

Chapman's¹² method makes use of an organism originally isolated from raw cane sugar and referred to as *Bacterium C*. This is inoculated into broth agar to which known and varying amounts of a 0.5% hop infusion have been added. The contents of the inoculated tubes are poured on to sterile Petri dishes and the antiseptic power of the infusion measured by the quantity required actually to inhibit growth. In the *Lactobacillus delbrückii* method devised by Hastings, Pyman and Walker,¹³ the measurement of antiseptic potency is based on the restriction of lactic acid production by measured volumes of a 0.25% infusion, instead of on determination of the lethal quantity. The two methods give results in substantial agreement.

The very serious drawback to biological methods arising from the fact that the virility or resistance to antiseptics of bacteria varies from generation to generation may be overcome by standardising the cultures against some known antiseptic. Phenol was suggested for this purpose by Chapman.¹⁴ The biological analysis would then become substantially a comparison between the toxic action of the hop infusion and phenol.

Shimwell and Kirkpatrick¹⁵ have studied the identity of *Bacterium X* and *Bacterium C*, with results that appear to show that no cultures of Brown's *Bacterium X* have been preserved. The culture in the Lister Institute collection is a strain of *Bacillus cereus*, one of the commonest aerobic, spore-forming species, prevalent in air, dust, etc., which they propose to distinguish as var. *arborescens*. *Bacterium C* was also found to belong to the same group, and for it they proposed the name *B. cereus* var. *rubicundus*. These are both more sensitive to hop antiseptics than *L. pastorianus*, to which the original *Bacterium X* was apparently allied, but are incapable of growing in media having a hydrogen ion concentration greater than p_H 5, such as unhopped

beer, though they develop rapidly in unhopped wort with a higher p_H value.

(271) The Log Phase Method of Analysis.

This method was devised by Walker, Hastings and Farrar¹⁶ for the quantitative comparison of very small degrees of antiseptic potency. It is based on restriction of lactic acid formation by *Lactobacillus bulgaricus*, which can be isolated from St. Ivel cheese. It was termed the Log phase method because it is used to measure acidity produced during the logarithmic phase of the growth of the bacterium in wort. The multiplication of micro-organisms in a suitable nutrient liquid has been divided into four well-defined phases: (1) An initial lag phase, in which the cell increase is very slow. (2) A period of maximal or constant growth, in which the logarithms of the number of cells present fall on a straight line when plotted against time, that is one cell produces another, these two become four and these four become eight in equal successive intervals of time. This is called the logarithmic phase. (3) A stationary or resting period and (4) a period during which the number of living organisms progressively diminishes until all have died. With certain micro-organisms the increase of some specific metabolic product can be measured against these periods and, when plotted, the curve obtained is parallel to the growth-time curve during the logarithmic phase, though it continues to increase after the growth curve has commenced to descend. Lactic acid is produced after this manner by *L. bulgaricus* and the quantity formed can be used as a measure of bacterial growth during the logarithmic phase or the reduction in acid production may be used as a measure of the restriction of growth caused by the presence of an antiseptic.

The method based on these principles is much more delicate than the previously described biological methods for comparing antiseptic powers and makes possible a comparison of the antiseptic potencies of worts or beers at different times during fermentation, storage, etc., as well as of hop decoctions. It is carried out by inoculating 99 ml. of 1,050 sp. gr. wort with 1 ml. of a vigorous 24-hour culture of *L. bulgaricus*, containing 2×10^8 organisms per ml. as denoted by a p_H value of 3.70. 1 ml. of the diluted culture, containing 2×10^6 organisms, is transferred to each of several flasks containing 200 ml. of wort at 30° C. These flasks are incubated for 6 hours, to ensure that the logarithmic phase of growth has commenced, when the appropriate quantity of wort or beer or 1 ml. of a 0.5% hop decoction is added, one flask being used as control. After a further incubation of 17 hours, the worts are electrometrically titrated back to their initial p_H . The differ-

ence between the number of ml. of N/10 NaOH required in the control and in the test flasks represents the restriction in acid production caused by the antiseptic present.

In common with all other bacteriological methods, the log phase method depends on the virility of the culture against which the antiseptic potency is measured. Consequently each analyst must standardise his own culture by constructing a curve for the production of lactic acid with the particular strain of bacteria used, in presence of known weights of humulon. Walker and Parker¹⁷ found that 50% restriction of acid formation was caused by 360 mgm. of phenol or 0.155 mgm. of humulon under their experimental conditions. If phenol is used for standardising the virility of the cultures, the results can be compared with the above and determinations calculated to a common basis. Humulon is the best standard of reference for the antiseptic potency of wort, the "humulon equivalent" of which may be expressed by the quantity of humulon required to produce the same restriction as 1 ml. of the wort multiplied by 1,000.

Examples of the application of the Log phase method for measuring the relative preservative power of hops are given in Table 104, the acid production being measured by N/10 NaOH under the standard conditions laid down by Walker, Hastings and Farrar.

TABLE 104.—EXAMPLE OF LOG PHASE METHOD

Sample	ml. N/10 NaOH to neutralise acid produced	Restrictions in acid production	Restriction as % of acid in control	Relative re- strictions of antiseptic values.
Control ..	15.0	—	—	—
Hop A ..	8.0	15.0 — 8.0 = 7.0	47	100
Hop B ..	9.5	15.0 — 9.5 = 5.5	37	78
Hop C ..	10.0	15.0 — 10.0 = 5.0	33.3	70.8

(272) Effect of Hydrogen Ions on the Antiseptic Power of Hops.

Fernbach and Stoleru¹⁸ found that the antiseptic power of hops varied greatly at different hydrogen ion concentrations, being very great between p_H 5.5 and 6.8, but almost disappearing when the p_H of the medium is between 7.4 and 8.4, while at the last value bacteria can grow in the hop decoction itself. These statements have until quite recently been accepted literally as applying to all bacteria and care has been taken that the p_H value of media used in biological analyses should not much exceed 6.0. Shimwell,³ however, points out that they are far too

sweeping and were based on experiments with the Gram-negative *Es. coli* (*B. coli commune*) only, which like other Gram-negative species is very resistant to hop antiseptics. It was indeed shown in other experiments that growth of the Gram-positive *B. subtilis* was inhibited by quite small quantities of hop antiseptics at p_H 8.5. Shimwell now shows that some bacteria are completely inhibited at p_H 8.0 by hops at the rate of 2.7 lb. per barrel, which is considerably less than is required to prevent the growth of *L. pastorianus* at p_H 4.2. The hitherto-accepted statement that hops only exert an antiseptic action when the medium has an acid reaction is consequently inaccurate.

The degree to which hop antiseptics are activated at varying p_H values differs widely with different bacteria. It does not follow because one species is more sensitive than another at one hydrogen ion concentration that it will still be more sensitive at another. Shimwell, indeed, found, in the case of *Es. coli* and *L. pastorianus*, that an increase of acidity reversed the order of sensitivity. The former, though unaffected by 0.5% hops at p_H 5.18, was found to be completely inhibited by the same hop concentration at p_H 4.4, whereas *L. pastorianus*, though strongly retarded by 0.5 % hops at p_H 5.18, still grew at p_H 4.4 with the same hops. This does not appear to be due to the acid tolerance of *L. pastorianus* as the high acid bacteria *L. bulgaricus* and *L. delbrückii* are completely inhibited by very small concentrations of hop antiseptics at p_H 5.18, while certain acid-intolerant species withstand very high hop rates even at this low p_H value.

It would appear very difficult, if not impossible, to predict the behaviour of different bacteria under the widely varying conditions prevailing in wort and beer, because the extent to which the antiseptic substances and hydrogen ion concentration severally contribute to the total antiseptic effect varies at different rates with different species. As an example of the varying rate of contribution of hydrogen ions to the total toxicity, Shimwell noted that whereas a decrease of hydrogen ion concentration from p_H 4.4 to 5.18 at a hop concentration of 0.5% decreased the antiseptic action towards *Es. coli* from complete inhibition to complete inactivity, it was necessary to raise the p_H to well on the alkaline side of neutrality before toxicity disappeared in the case of some Gram-positive bacteria.

(273) Fractionation of the Hop Resins.

The first method of fractionation consisted in separation of the soft and hard resins, according as they were soluble or insoluble in light petroleum spirit. A further fractionation of the soft

resins, based on Hayduck's separation into α - and β -resins, was developed by Siller¹⁹ and became the basis of the methods of gravimetric analysis used to-day. If the solution obtained by extracting ground hops in a Soxhlet apparatus with ether is evaporated to remove the solvent and the residue treated with warm methyl alcohol, the hard and soft resins are dissolved, leaving a residue containing wax-like substances. A yellow precipitate of the lead salt of humulon is obtained by adding a solution of lead acetate in methyl alcohol to the solution at about 60° C. This precipitate can be decomposed by sulphuric acid or hydrogen sulphide, giving crystalline humulon in fair yield. Complete separation of humulon cannot be obtained, on account of its instability and the readiness with which it is converted into resin in the presence of impurities. Siller found that the precipitate had a lead content of 36.65%, the factor for converting the weight of lead salt into humulon being 0.6319. The quantity so obtained is frequently referred to as the α -resin of the hops, though it is better to describe it as humulon.

Lupulon, together with resins formed from it and from humulon, which do not form insoluble lead salts, remain in solution in the methyl alcohol after filtering off the lead salt of humulon. Lupulon can be prepared in a crystalline form²⁰ from the alcoholic solution by extraction in light petroleum, followed by processes of purification involving extraction in dilute alkalis, acidification and extraction in ether.

The chemical relationships between the original acids and the resins formed from them and the mechanism of the transformations, which are generally held to be due to oxidation, are far from being elucidated but the great complexity of the changes has given rise to the suggestion by Kolbach²¹ that division of the soft resins into α - and β -resins is inadequate. Windisch, Kolbach and Schleicher²² found that humulon was converted by oxidation to hard resin when it was boiled in water which was either neutral, slightly acid or slightly alkaline, but gave soft resinous products when boiled in a citrate buffer solution at p_H 6.2 in absence of air, the transformation to soft resin being more rapid in alkaline liquids. This soft resin was found to be more acid than humulon, more soluble in water or wort, but not precipitated by lead acetate. It, however, resembled humulon in bitterness and antiseptic properties. The soft resin formed from humulon by boiling in absence of air and that produced during storage or boiling in air have been distinguished as transformation or boiling product and oxidation product, respectively.

The fraction remaining in solution in methyl alcohol may thus be supposed to consist of lupulon, at least two different types of

resin formed from humulon and another resin derived from lupulon. These together are generally referred to as the β -resins or β -fraction of the soft resins. Kolbach further suggested that the final products of change or hard resins should be divided into α - and β -hard resins, derived from humulon and lupulon respectively, and that the term γ -resin should be abandoned as synonymous with hard resins and only used for resins formed from the hop oils.

Walker²⁰ found that the β -fraction separated from good quality hops contained 17 to 20% of crystalline lupulon, 39 to 43% of resins of acidic character and about 41% of adventitious material. A Golding hop with 5% of β -fraction would thus contain only about 1% of lupulon. It is on account of the high proportion of other substances that the relative antiseptic power of the β -fraction is less than that of the α -fraction, although lupulon is a more powerful antiseptic than humulon. Lupulon is readily converted to resin in presence of oxygen and its proportion in the β -fraction gradually diminishes during storage of the hops until little or none remains. Pure humulon is fairly stable but moisture and impurities accelerate its decomposition, so that the humulon of hops is more readily resinified during storage than the pure acid.

The resin fractions may be summarised as follows :

(1) *Soft resins* soluble in ether, methyl alcohol, ethyl alcohol, light petroleum spirit, hexane or trichlorethylene. They are divided by precipitation by lead acetate in methyl alcohol into :

(a) Humulon, the so-called α -resin or α -fraction of the soft resins, precipitated as the lead salt.

(b) The so-called β -resins or β -fraction of the soft resins, remaining in solution in the methyl alcohol and consisting of lupulon with α -resins (transformation and oxidation products) and β -resins.

(2) *Hard resins* soluble in ether, methyl alcohol, ethyl alcohol and trichlorethylene but insoluble in light petroleum spirit and hexane, divided into :

(c) α -hard resin, formed from humulon.

(d) β -hard resin, formed from lupulon.

(e) γ -resin, produced from hop oils.

The relative proportions of the three main fractions vary very considerably in different hops, but approximate percentages on the total ether-soluble resins in high quality fresh hops are :

<i>Soft resins</i>	α -fraction (humulon)	30–45% of total resins		
	β -fraction	45–60%	„	„
<i>Hard resins</i>		10–20%	„	„

Walker tested the antiseptic powers of various fractions of the resins with several strains of bacteria isolated from sour beer and found that the antiseptic powers of humulon and the α -fraction were approximately the same and constant for all hops, while lupulon had twice the antiseptic value of humulon. The antiseptic value of hop constituents and the relative activity of humulon and lupulon vary very greatly with different bacteria and under different conditions. When tested with *L. bulgaricus* by the log phase method, Walker and Parker¹⁷ found the following relative restrictive actions, weight for weight, on lactic acid production. In these experiments the pure preparations were not heated and they were all immensely more effective than phenol.

					Relative antiseptic values (log phase method)
Humulon	4,000
Lupulon	28,000
β -fraction of the Soft Resins				..	7,200
Phenol	1

These remarkable figures may bear little relation to the antiseptic potency of the resin existing in hopped wort, but the inhibiting effect of 2 ml. of a 1% solution of phenol on *Bacterium C* in Chapman's method of analysis is equalled by that of 2 ml. of a 0.5% decoction of a very moderate hop. Since only very small quantities of the active constituents of the hop can exist in the decoction, their antiseptic potency, even after boiling, must be much greater than that of phenol. There is also an apparent discrepancy between the relative potency of humulon and the β -fraction as determined by the log phase method and the ratio 3 : 1 used in gravimetric analysis. (Section 275.) This is explained by the different methods of solution or extraction and the varying effects of heat, moisture and oxygen on humulon and lupulon.

(274) Gravimetric Methods of Analysis.

For many years the only methods available for assessing the preservative power of hops were based on determination of the total soft resins extracted by light petroleum spirit or by measurement of the acidity of the extract. These were developed after it was proved that the hard resins had no antiseptic properties and that the soft resins contained acidic substances to which these properties were attributed. In Lintner's²³ acidity determination, 10 grams of hops were extracted in 800 ml. of boiling light petroleum spirit for 8 hours under a reflux condenser and the volume made up to 505 ml., the 5 ml. being assumed to be the

volume occupied by the hops. 100 ml. of the extract was made up to 180 ml. with 96% alcohol and titrated with N/10 KOH in 90% alcohol with phenol-phthalein as indicator. A blank was used to correct for acid in the solvents. The result was expressed as monobasic acid by multiplying the number of ml. of KOH required by 0.4. The method of extraction in light petroleum spirit under a reflux condenser, developed by Briant and Meacham,²⁴ was generally used in England until it was shown by Adrian Brown and others that the antiseptic value of hops was not proportional to the weight of soft resins obtained on evaporation of the extract. It was some years, however, before Siller's method of fractionating hops by precipitating humulon in the form of its lead salt was worked out by Ford and Tait²⁵ and shown to provide a much more reliable method of hop valuation.

The methods of Ford and Tait, Walker and Hastings²⁶ and of Wöllmer,²⁷ are based on the original method devised by Siller. That of Wöllmer has been adopted as a Convention method by the Analysis Committee of the German Brewing Institutes, while Ford and Tait's method is generally used in England.

In Ford and Tait's method the hard and soft resins, together with the small quantity of wax, oil and chlorophyll associated with them, are first extracted from the ground hops by warm ether in a Soxhlet apparatus. The ether is removed from the resinous material, which is then dissolved in methyl alcohol leaving an insoluble residue of wax-like substances. Pure methyl alcohol must be used for this purpose as the lead salt of humulon is more soluble in denatured spirits or in ethyl alcohol. The α -fraction of humulon is determined by precipitation with lead acetate in a part of this solution and the total soft resins in another part by extraction in light petroleum spirit. The difference between the total soft resins and the α -fraction gives the β -fraction. Excess of lead acetate solution, in which the humulon lead salt is also slightly soluble, is carefully avoided. Kolbach and Kleber²⁸ have since found that precipitation of the lead salt is also hindered by the resins, accounting for slow precipitation and low results with old hops. This is attributed to the greater acidity of the resins in comparison with humulon, and can be counteracted by small additions of caustic potash to bring the p_H of the solution to that of humulon.

Wöllmer's method is identical in principle but differs in details. The original extraction is made by shaking the ground hops with cold ether. This extracts rather less than warm ether but the difference is due to inactive substances. A methyl alcohol solution of the total resins is then obtained, as in Ford and Tait's method, and the total resins (hard and soft) found by evaporating a portion

of this solution to dryness. The soft resins are then extracted from another portion of the methyl alcohol solution by means of a definite hydrocarbon, hexane, instead of the rather indefinite mixture known as light petroleum spirit. The humulon and β -fractions are determined as in Ford and Tait's method.

The use of ether is avoided in Walker and Hasting's method by extracting the total resins from hops by shaking with cold methyl alcohol. The humulon cannot be precipitated directly from this solution, since it contains other substances which give a precipitate with lead acetate. The soft resins are consequently extracted from the methyl alcohol solution by shaking with light petroleum spirit, after which the analysis is continued as in the Ford and Tait method.

The readiness with which humulon and lupulon are resinified is recognised in all these methods of analysis and every care is taken to prevent this by excluding air and keeping the temperature low when the ether solution is evaporated to dryness. The colloidal properties of the resins also occasionally create difficulties when the methyl alcohol solution, after dilution with water, is extracted with light petroleum spirit.

(275) The Preservative Value of Hops.

The gravimetric analyses actually determine the quantities of the α - and β -fractions of the soft resins in a given weight of hops. If the relative antiseptic values of these fractions were constant and known, it would be a simple matter to express the relative antiseptic powers of a series of hops in terms of one or other of the fractions. Since the α -fraction is almost pure humulon, it is evidently indicated as the basis of reference. In view, however, of the variable composition of the β -fraction, it would seem impossible to find definite relative values for the antiseptic potency of the α - and β -fractions applicable to all hops. Walker²⁹ nevertheless came to the conclusion from biological determinations of the quantities required to arrest growth in cultures of various bacteria isolated from sour beer that, weight for weight, the antiseptic potency of humulon or of the α -fraction of most good quality hops was about three times as great as that of the β -fraction, the tests being made in culture media which had been sterilised after addition of the antiseptic, before addition of the bacteria.

On this basis the relative preservative value of different hops would be expressed by $\alpha + \frac{\beta}{3}$ in which α and β represent the percentages of the two fractions. This relation is generally accepted in analyses in this country and the figure so obtained is

usually multiplied by 10 to avoid decimals in the results. The relative preservative value of hops is then expressed by:—

$$\text{P.V.} = 10 \left(\alpha + \frac{\beta}{3} \right)$$

On the other hand Wöllmer³⁰ found that beers produced from worts which had been boiled with humulon kept sound for months, whereas others boiled with β -fraction soon became sour. He found that the bittering power of the α -fraction was about 9 times as great as that of the β -fraction and was, together with the antiseptic power, derived almost exclusively from the humulon and its first decomposition products. As a result of these findings it has become customary on the Continent to express the "brewing value" of hops by the expression $\alpha + \frac{\beta}{9}$. (See Sections 302 and 308.)

The antiseptic potencies of the α - and β -fractions vary with the p_H value of the medium, just as does the total toxicity of the hop extractives and also, no doubt, with different bacteria. Windisch, Kolbach and Schüren³¹ examined this with *L. delbrückii*. The antiseptic power of humulon isolated from the lead salt was found to vary more widely with p_H than that of the β -fraction separated from it. Under the conditions of these experiments the relative antiseptic potencies of humulon and β -fraction in regard to *L. delbrückii* were as 14 : 4.5 at p_H 5.6 in wort, agreeing well with Walker's 3 : 1, but at the p_H value of beer the results, 8 : 0.75, were in closer agreement with Wöllmer's ratio of 9 : 1.

These authors suggest that the varying influence of hydrogen ion concentration depends on the different strengths of the α - and β -acids. It may be supposed that these exist in hopped wort partly in the free state and partly as less strongly antiseptic alkaline salts. The relative proportion of acid and salt would depend on the strength of the acids and less of the stronger acid, humulon, would exist in the free state in alkaline solutions than is the case with lupulon. Wöllmer³² found by tests in dilute phosphate buffer solutions that the solubility of humulon increased more than that of lupulon as the acidity diminished. The solubility of humulon, at p_H values of 4.94, 5.59 and 6.24, was 65, 244 and 740 mgm. per litre respectively, while that of lupulon was 8, 8, 16 and 48 mgm. per litre, at p_H values of 4.95, 5.59, 6.24 and 6.98.

At the p_H value of beer lupulon appears to be practically insoluble, while, according to Kolbach, only 8 mgm. of humulon can be dissolved in a litre of a dilute acetate buffer solution at p_H 4.0. Wöllmer, however, found that 60 mgm. per litre of solid matter derived from humulon and 13 mgm. per litre derived from

lupulon are dissolved by boiling in water for 2 hours. These quantities must represent transformation products of the bitter acids. The bearing of these points on the behaviour of hop resins in the copper will be dealt with in the chapter on wort boiling.

(276) Colorimetric Analysis of Hops.

Guthrie and Philip³³ found that uranium acetate gave an intense orange-yellow colour with humulon in methyl alcohol solution and a much less intense colour with β -fraction solutions of equal concentration. On this they based a rapid method for comparing the resin content or preservative value of hops by comparison of the colours produced in methyl alcoholic extracts of the hops and standard solutions of humulon. The results, expressed in terms of humulon percentage required to give a colour match, compared well with preservative values determined by Ford and Tait's method.

(277) Comparison of Biological and Gravimetric Grading.

It will be observed that the term "relative preservative value" has been used in connection with both methods of analysis, suggesting no more than comparative values for different hops. The term "potential preservative value" might apply to the results of gravimetric analysis, in that they are absolute in the sense that they measure quantities of two antiseptic fractions and refer the antiseptic values of hops to that of humulon, under the assumption that constant relative potencies, such as 3 : 1, can be assumed for unit weights. The lack of accuracy in this assumption is recognised, but it is not a simple matter to check it by biological tests with bacteria, since these differ so widely in their sensitiveness to hop antiseptics and because there is no assurance that a standard method of extracting hops for biological assay will have the same or proportional extracting and destructive effect on the antiseptic substances of all hops. There is thus no certainty that the results of biological analyses can give a truer estimate of the relative preservative value of hops than those obtained by chemical analysis, even when the virility of the culture is standardised against phenol or other pure antiseptic. A great advantage of chemical methods is that they give absolute figures at any time for the quantitative relationship of the α - and β -fractions as they exist in the hops. It should be possible to derive information from these on the condition and treatment of the hops, from the known behaviour of the resins during ripening, drying and storage, and on their influence on the stability and flavour of

the beer from what is known of the changes in the resin fractions during boiling and fermentation. The comparative figures for the relative preservative value of the hops, obtained by the two methods, are based on different considerations. The one gives quantitative figures for two fractions of the resins. The other measures the antiseptic potency of whatever substances can be extracted by boiling in water. Despite this difference in principle, the results obtained are very concordant for hops of good brewing quality, analysed within about a year of harvest, and it will generally be found, though exceptions are met with, that the preservative values of a series of hops are placed in the same order whichever method of analysis is used.

The figures in Table 105, from analyses by Walker and Hastings, show the concordance in the analyses of six samples by Ford and Tait's gravimetric method, by Chapman's biological process and by the log phase method. The values found by the various methods are on entirely different scales, so that it is necessary in comparisons of this kind to express those found for one of the hops as 100 in each case, giving the other values in proportion.

TABLE 105.—COMPARATIVE ANALYSES OF HOPS BY GRAVIMETRIC AND BIOLOGICAL METHODS

Hop	Gravimetric, Ford and Tait			Relative PVs. A taken as 100		
	Humulon %	β -fraction %	$\alpha + \frac{\beta}{3}$	Ford & Tait	Chapman	Log phase
A	7.89	8.91	10.86	100	100	100
B	6.50	8.95	9.49	87.4	100	97
C	6.68	7.62	9.22	84.9	94.6	88
D	6.38	8.17	9.10	83.8	85.7	83.6
E	5.07	8.83	8.01	73.8	75	73.2
F	3.61	8.80	6.54	60.2	54.5	49.7

(278) Validity of Analyses.

The bacteria selected for the biological assay of the preservative value of hops have been selected on account of their sensitiveness to the antiseptic substances present. The methods are consequently open to the criticism that these are not likely to be among the bacteria that will develop in beer and that those which can grow must be more or less resistant for some specific reason or because they have acquired some degree of immunity by acclimatisation to life in a medium containing hop extractives. On the other hand the values for the relative antiseptic value of hops, based on quantitative determinations of humulon and the

relative antiseptic potencies of this substance and the β -fraction, can hardly be supposed to give a measure of the antiseptic substances existing in beer. Great changes occur in the resins during copper boiling and humulon does not exist in the beer as such. However reasonable these criticisms appear, there is a good deal of evidence that hops which are graded highly by either method will produce a beer that is biologically more stable than low graded hops. The usefulness of the results depends on whether they arrange a series of hops in order of preservative value corresponding with their actual effects on the stability of beers under identical conditions of infection and in the absence of any other variations which might influence the growth of micro-organisms. Such conditions are difficult to realise but sufficient evidence, based on tests of beer stability, has been obtained to confirm Ford and Tait's²⁵ original claim in respect of the majority of hops of the quality used in brewing.

"Considering the impossibility of expressing the stability of beers on a numerical basis, the correlation of the analytical valuation and the biological results was highly satisfactory and provided sufficient evidence to convince us that the analytical method, whilst not on a very sure scientific foundation, gives results which enable hops to be classified according to their relative preservative values, provided of course that they are used in certain limiting proportions."

Owing to the decomposition of lupulon during drying and its gradual resinification during storage, the antiseptic potency of a given weight of β -fraction as compared with that of an equal weight of humulon must fall very considerably and the expression $10 \left(\alpha + \frac{\beta}{3} \right)$ which was based on experiments with dried hops a few months old, cannot apply either to green or old hops. It gives much too low a value for green hops and suggests a somewhat higher relative preservative value for old hops than they actually possess. The gravimetric analysis of old hops is, however, influenced more seriously by the incomplete precipitation of humulon in presence of excess of resins. It gives unduly low results. Biological methods usually give a considerably higher preservative value with old hops and this is confirmed by brewing experience. Analyses of a Tutsham hop by Hastings and Walker²⁴ when green and after drying in a current of air at 104° and in the ordinary commercial manner, with figures obtained by biological grading, illustrate this (Table 106).

In order to afford a true comparison between the preservative value of hops containing varying percentages of moisture, it is usual to calculate the results of analyses to moisture-free hops.

TABLE 106.—ANALYSES OF GREEN AND DRIED HOPS

Hop sample	Moisture %	Per cent. on dry hops		P.V. $10\left(\alpha + \frac{\beta}{3}\right)$	Biological grading (on dry)
		Humulon	β -fraction		
Green hops	78.0	3.38	9.10	64.1	237
Dried at 104° F. ..	6.70	3.88	8.77	68.0	133
Commercially dried ..	11.43	4.21	8.62	70.8	100

OTHER HOP CONSTITUENTS

(279) Hop Oil.

The relatively small quantity of essential oils contained in hops is responsible for their fragrance and thus, in no small degree, for their brewing value. They occur chiefly in the lupulin and can be separated from it or from the cones by steam distillation or solution in alcohol or ether. Whole cones yield from 0.2 to 0.5% of oil when submitted to steam distillation. The oil thus obtained has a specific gravity of between 0.84 and 0.88 with an $[\alpha]_D$ of from -0.08° to $+0.60^\circ$. It is soluble in water to the extent of about 1 part in 20,000 but is more soluble in dilute alcohol and completely dissolves in 95% alcohol. Oxidation may lead to the production of *iso*-valeric acid, which is sometimes detected by its odour in old hops. Under ordinary atmospheric pressure the oil commences to boil at about 150° C. (302° Fahr.), the boiling point rapidly rising to 230° C. (446° Fahr.) between which temperature and 270° C. (518° Fahr.) most of it distills, leaving a resinous mass resulting from decomposition of higher boiling fractions. To prevent this decomposition the oil is distilled under partial vacuum and can be fractionated in this way. Chapman³⁵ has isolated and identified numerous different essential oils in the mixture. These are detailed in Table 107. The aromas of hops from different sources no doubt depend to a considerable extent on varying proportions of the constituents but they are associated with such slight differences in composition of the oils that available methods have proved insufficient to detect the cause of variations. During storage, part of the hop oils are converted, probably by oxidation, to neutral resinous products with an unpleasant flavour. The preservative value of hops was at one time associated with the oils but they are now generally believed to have no antiseptic activity. This should not be accepted as proved. Risler's³⁶ work on the essential oils of various plants, indeed, suggests that further investigation is desirable. This author proposed the term *abiotaxines* (from the Greek *taxein*, to fix) for complexes

resulting from the mixture of volatile oils, which have fugitive antiseptic properties, with resins, which lower the vapour tension of the oils and stabilise their antiseptic action over years.

TABLE 107.—CONSTITUENTS OF HOP OIL

	Formula	Sp. gr.	Boiling point C.
Myrcene	$C_{10}H_{16}$	0.801	167°
Linalool	$C_{10}H_{18}O$	0.872	197°
Geraniol	$C_{10}H_{18}O$	0.88	229°
Linalyl isononoate	$C_{27}H_{44}O$	—	—
Humulene	$C_{15}H_{24}O_9$	—	264°
Luparone	$C_{15}H_{22}O$	—	Above 264°
Luparenol	$C_{15}H_{24}O$	—	"
Luparol	$C_{16}H_{26}O_2$	—	"

Humulene and myrcene are the most important constituents, forming 80 to 90% of the distilled oil from fresh hops. Humulene, which accounts for varying proportions, around 50%, is a colourless oil belonging to the group of sesquiterpenes. When pure it has very little odour and thus acts as a diluent of the more fragrant fractions. Its quantity may vary slightly with the origin of the hops but an increased percentage in distilled oils mainly depends on reduction in the quantity of other constituents through oxidation and resinification. Myrcene is a colourless mobile liquid of characteristic odour but different from that of the whole oil, to which it gives a penetrating character it would not otherwise possess. It is an unsaturated open chain hydrocarbon which rapidly oxidises and polymerises on exposure to air, giving a viscous, colourless syrup. As a result of this, freshly distilled oil, when exposed to air, rapidly becomes more and more viscous and less soluble in alcohol. In new hops myrcene accounts for 30 to 40% of the oil, but that distilled from old hops may contain little or none.

Among the constituents which occur in smaller quantity, but may have appreciable effects on the odour of the oil, are linalool, geraniol and linalyl isononoate. Linalool is an unsaturated open chain alcohol. Geraniol has the same molecular formula as linalool. It has a very pleasant odour but is only a very minor constituent of the oil. Linalyl isononoate, like many other esters, has a very powerful odour and, although it occurs in very small quantity only, has a material effect on the aroma.

The higher boiling fractions were separated by distillation under such low pressures as 2 and 3 mm. of mercury. Luparone is a ketone with a very pleasant aroma, boiling at 75° C. under 3

mm. pressure. Luparenol is a viscous, odourless, colourless liquid, with the constitution of an unsaturated sesquiterpene alcohol. It boils at 127° C. under 3 mm. pressure. Lupaol is a phenolic ether, a pale yellow liquid with slight but pleasant odour, boiling at 123° C. and 2 mm. pressure. Very little of these high boiling constituents can occur in commercial oils but they may have some effect on its aroma.

(280) Hop Oil in Brewing.

Hops are selected very largely on account of their aroma and the condition of the oils is generally the surest guide to the general quality of samples as judged by physical examination. Any objectionable odour will be communicated to their non-volatile oxidation products and to the beer. They have no preservative value, but lack of aroma is clear evidence of loss of some of the other valuable hop constituents. Despite the very high boiling point of some of the fractions, hop oil is readily distilled in steam and in consequence a large proportion must be evaporated from the wort during boiling. Chapman placed the loss at 90% or over when the wort was boiled for 2 hours. The remainder is converted into resinous substances which, fortunately, possess much of the aroma and flavour of the essential oils from which they were produced by oxidation and polymerisation. Even when some of the hops are added shortly before turning out of the copper, only very little more of the essential oil remains in the wort. Much greater use is made of their flavouring properties by dry hopping, but the slight solubility of the oil in wort or dilute alcohol makes it essential that the hops remain in contact with the beer for some weeks to obtain the best results. The small quantity dissolved is quite sufficient to give the desired flavour, as this is more apparent when essential oils are at high dilution.

The advantages of dry hopping do not depend solely on the aroma which the oils impart to the beer but also on dispersion of part of the resins with their preservative substances and to beneficial action on condition, which appears to be due in part to the action of diastatic enzymes contained in the hops on difficultly fermentable carbohydrates in the beer. The cones themselves have a mechanical use in the casks. They assist fining and, by preventing the settlement of yeast in a hard deposit, facilitate the subsequent cask washing.

(281) Commercial Hop Oils.

The present methods of using hops are no doubt uneconomical, in respect of the utilisation of their essential oils, and dry hopping

is troublesome and not very effective with chilled beers in tanks, unless a strongly flavoured hop is used, on account of the comparatively short storage frequently adopted and the loss of hop flavour during filtration. Commercial hop oils extracted from fresh hops are conveniently and successfully used for this purpose, 15 ml. being sufficient for 130 barrels. The oil may also be used in cask beer which is not kept long enough to extract the dry hops. 3 or 4 drops per barrel are commonly used, 3 drops per barrel being approximately equal to 1 ml. per 10 barrels. Before use the oil is mixed with 5 times its volume of 90% alcohol or rectified spirits. The required quantity for a barrel is then mixed with a pint of the beer and added to the cask, which is well rolled. For use in tanks, the measured quantity of alcoholic solution is mixed with two or three gallons of the beer and pumped into the tank. The oil may also be used as an emulsion in priming solutions.

(282) Hop Extracts.

Extracts of hops are made with various solvents in which the resins, tannin and hop oils are soluble. Thus a low boiling-point solvent, such as ether, extracts the resins and oils and when evaporated off leaves the oils with the extract. A higher boiling-point solvent, such as alcohol, also extracts resins and oils but on evaporation the oils are removed with the alcohol. The tannin can be extracted from the residue by means of water. Hop extracts which retain the resins in an active condition are useful for brewing in countries to which export of hops would be very expensive. The humulon is resinified during manufacture, but biological tests show the antiseptic potency of hop extracts is substantial and is preserved from deterioration by air-tight packing.

(283) Hop Tannin.

Tannin is a generic name for a group of substances widely distributed in plants and showing certain characteristic properties. Among these are an astringent flavour, ready solubility in hot water, giving colloidal solutions, and ability to precipitate proteins from solution. The last reaction is analogous to that made use of in tanning, by which the proteins of hide are converted into insoluble and very resistant products. It also plays an important part in the behaviour of hops during copper boiling, when the tannin derived from the petals and strigs, and amounting to between 2 and 5% of the weight of the hops, combines with the proteins of the wort and assists in their precipitation. Tannin also forms complexes with some of the higher protein degradation products, generally referred to as tanno-peptones. These are soluble in

hot wort but come out of solution as the wort is cooled or during fermentation and storage of the beer. These reactions are more fully dealt with in the chapters on wort. Tannins also give a black colour with ferric salts, a reaction occasionally noticed if sugars containing more than the usual very slight trace of iron are used in the copper, when the spent hops become dark in colour. Oxidation of tannins gives rise to formation of dark reddish-coloured products known as phlobaphenes which have an influence on the colour of beer. These are also produced by boiling the solutions of tannin. They give precipitates with soluble proteins that are not soluble in hot wort. Their production in the copper and combination with or adsorption on wort proteins is consequently of importance at that stage of brewing.

(284) Soluble Nitrogen of Hops.

Hops contain between 2 and 4% of nitrogen of which about 0.4 to 1.0%, with a rough average of 0.6%, is soluble in wort. Potassium nitrate is present, while asparagine, choline and betaine have been detected but no alkaloids related to morphine, the presence of which has sometimes been assumed, could be found by Chapman.³⁷ Brown found that 61% of the soluble nitrogen was assimilable by yeast. Chapman gave the following average composition of the soluble nitrogen compounds :

Soluble proteins and proteoses, 9.5%.

Ammonium salts and amides, 20.22%.

Amino-substances, 19.5%.

Bases and unclassified nitrogen precipitated by phosphotungstic acid, 43.5%.

Unclassified nitrogen by difference, 7.28%.

As a result of the extraction of permanently soluble nitrogen from the hops, the nitrogen content of boiled hopped wort is almost the same as that of the same wort previous to boiling, the quantity of nitrogen precipitated being usually balanced by that extracted from the hops.

(285) Pectins.

It is only recently that attention has been drawn, by Fink³⁸ and his collaborators, to the existence of a considerable quantity of pectins in hops. Substances of this nature occur as a kind of cementing material among the cellulose fibres in the hop cones, of which they may constitute 12 to 14% on the dry weight. They are extracted by boiling in water and therefore, presumably, by wort, in which they would probably exist as hydrated pectin.

Fink states the quantity of the latter in wort hopped at the rate of 300 grams per hectolitre averages 18 to 25 grams per hectolitre. So far practically nothing is known in regard to variations in their quantity in hops at different stages of ripeness, in hops of different varieties or origin, nor in regard to the quantity extracted in the copper or to the changes they undergo there.

From what is known of the varying effect of extracts of under-ripe, ripe and over-ripe apples in jelly formation due to the pectins and the fact that under-ripe fruit is used with the best results, it might be expected that similar differences would exist in the pectin of hops according to their ripeness. The variety, place of growth, season and storage might also have their specific influences. These questions are at present entirely speculative and remain to be investigated. Practically nothing can yet be said about the changes in the pectins during boiling but it is known that increased acidity in general increases their dispersion. It is even impossible to say whether their presence in wort is helpful or injurious, although they probably have beneficial effects on some of the colloidal properties of beer.

(286) Summary.

The most important constituents of hops are included in the resins, the oils, tannins and pectins. The resins are divided into α - and β -soft resins, which are soluble in light petroleum spirit, and hard resins which are insoluble in that solvent. The hard resins are of no value in brewing, the antiseptic properties of hops depending largely on two acidic constituents of the α - and β -fractions, humulon and lupulon, and their first resinous derivatives. The bitterness of hops depends largely on the humulon and resins formed from it. Hop oils consist of a number of high boiling-point essential oils which are volatile in steam. They give the aroma to hops and to beer in which dry hops have been used. They also contribute to the aroma of beer through resinous products which still retain some of the original flavour. Tannin has an astringent flavour and assists in the precipitation of protein in the copper and combines with other protein derivatives, forming the cooler deposit. The pectins probably contribute to the colloidal properties of wort. Hops also contain a small percentage of soluble nitrogen, a proportion of which is assimilable by yeast. The amount of nitrogen extracted from hops by boiling with wort almost exactly counterbalances that removed from the wort by coagulation.

The antiseptic value or preservative power of hops is determined either by gravimetric analysis of the resins or by biological tests

with bacteria. It is expressed in terms of the percentage of α - and β -fractions of the soft resins by the expression $10 \left(\alpha + \frac{\beta}{3} \right)$.

The values obtained by either method are relative, arranging hops according to their relative antiseptic potencies, and their utility depends on this order corresponding with the stability of the beers produced from the hops. There is good evidence that this relationship holds in practice for the majority of hops normally used in brewing.

Hop antiseptics have very varied influence on the growth of different bacteria. The antiseptic potency appears to correspond with the behaviour of the bacteria towards certain staining methods. Thus Gram-positive bacteria are sensitive to hops, while Gram-negative bacteria are relatively resistant. Humulon and lupulon are immensely more potent in respect of the former than phenol. The antiseptic power of hops is also materially influenced by the hydrogen ion concentration of the medium in which the bacteria exist.

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CHAPTER XVII

TYPES OF HOPS AND THEIR BREWING VALUE

TYPES OF HOPS

(287) Varieties of Hops.

Although the cultivated hops of Europe are considered to belong to one species, there are many strains that differ consistently in cultural habit, cone formation, aroma and other characteristics, such as the resin content of the cones and their development period, according to which they can be divided into early, mid-season and late hops. The different kinds are generally referred to as varieties and named after a grower, locality or some characteristic quality. To what extent crossing of different strains may have contributed to this is unknown, since the varieties have, in the majority of cases, been raised from a plant selected from a garden of established type, on account of some exceptionally good quality. This process of selection has gone on during the last two or three centuries in an endeavour to establish strains of improved quality, increased yield or greater resistance to disease. It has resulted in the cultivation in a large number of districts of hops of homogeneous type, particularly suited to the soil and climatic conditions, and also in the elimination of apparently well-established varieties and replacement by others which met with a greater measure of approval. In some instances where selection was directed primarily to increased yield, the quality has proved to be inferior. The different varieties have distinct characteristics but seasonal variations or differences due to management, disease or weather may be great and cause growths of a high class variety to fall below others that are normally inferior. On the other hand, advanced methods of culture or favourable climatic conditions may so raise the quality as to place a hop in a higher class than its variety normally attains. The characters attributed to different varieties must, consequently, be understood as applying to hops raised under normally favourable conditions.

(288) English Varieties.

During the Hop Control, established to meet the special circumstances of wartime, an attempt was made to group the different

varieties according to their quality and use and for purposes of price adjustment. The four groups differentiated were Goldings, Golding Varieties (G.V.), Fuggle's and Tolhursts. This grouping was satisfactory in many ways but the title Golding Variety was in some respects misleading, as the group included hops with little or no relation to Goldings. The difficulty of grouping the varieties is much increased by the variations in quality produced by methods of culture and conditions of soil and weather, but the scheme adopted did distinguish hops of more delicate flavour, such as is associated with the Goldings and generally held to make them particularly suitable for dry hopping purposes, and hops approaching them in character, the Golding Varieties, from the stronger Fuggle's or typical copper hop and the very prolific hops of lower quality, of which the Tolhurst was at that time very widely grown. The separation into dry hoppers and copper hops cannot be anything more than very general, depending on the quality of the particular growth as much as on its variety, since the Fuggle's is sometimes grown to such perfection that it may be preferred for dry hopping to a Golding which is not quite up to the average for its variety. Use of the terms dry hops and copper hops, consequently, does not imply that varieties suited for the former purpose are unsuitable for copper use but, merely, that they have the necessary characteristics of aroma and compactness for use in cask. They would generally be very suitable for copper use in beers of the highest class. Though there are difficulties in grouping hops in the manner indicated, the Hop Control names are retained here, as they are so generally understood in the trade.

(289) Goldings.

The typical hop of this class was selected from a garden of Canterbury hops by Mr. Golding at the end of the eighteenth century and the name is now used for a number of related varieties or strains grown in the most favoured localities, particularly in the East Kent, Worcester and Hereford districts. They are generally recognisable by the rounded shape of the cones and distinctive yellowing of the tips of the petals. Their aroma is delicate and preservative value generally high, but they do not yield such large crops as most of the coarser varieties. As a group, they are particularly appreciated for dry hopping but they are also largely used in the copper for high class beers, frequently blended with a Fuggle's. Among the related varieties are the original Canterbury Whitebine, frequently referred to as Canterbury Goldings, one of the oldest and best hops in cultivation. The photograph of this hop, Fig. 55, and also those of the Cobb and Fuggle's hop, were from hops grown at East Malling Research Station in 1935.



FIG. 55
CANTERBURY WHITEBINE OR GOLDING (HALF NATURAL SIZE)



FIG. 56
THE COBB (HALF NATURAL SIZE)

[Facing page 388]



FIG. 57
FUGGIE'S HOP (HALF NATURAL SIZE)

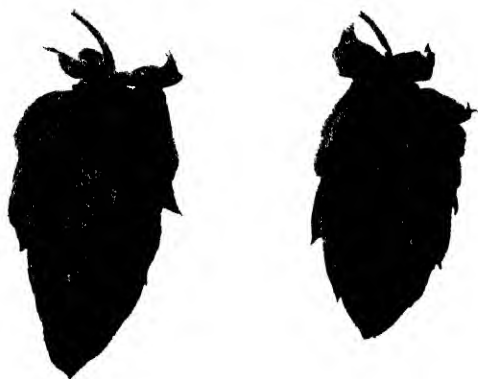


FIG. 58
BREWER'S GOLD

The Worcester Mathon, a mid-season hop named after the parish of Mathon near Worcester, and the Farnham Whitebine, the best known hop of the Hampshire district, are very similar to the Canterbury Whitebine and probably originated from the same stock. The Rodmersham Golding, selected by Mr. Mercer in 1880 from a garden of Golding hops at West Malling, is not quite equal to the Canterbury Golding in aroma. It is rather liable to canker and not extensively grown.

The Bramling is one of the best early ripening hops and was selected about 1865 from a garden of Goldings at Bramling, near Canterbury. It is a compact, medium-sized hop, round in section, with excellent aroma and good preservative value. It is widely grown in the Kent and Worcester districts. Amos' Early Bird is a selection from a Bramling garden, made by Mr. Alfred Amos of Wye in 1887. It is earlier than the Bramling, a better cropper but of not quite so good quality.

(290) Golding Varieties.

The Cobb, Fig. 56, was selected from a garden of Canterbury Whitebines by Mr. John Cobb, of Sheldwich, near Faversham, in 1881. It is a mid-season hop of good flavour but not very high preservative power. When of good quality, it is a useful dry hopper. The Tutsham has some of the growth characteristics of Goldings, being long branched and a Whitebine, but the cone is larger. It is a heavy cropper but not of very high quality, unless grown to perfection on suitable land.

(291) Fuggle's Hop.

Fuggle's, Fig. 57, is the typical copper hop. It is a mid-season variety, rich in lupulin and a heavy cropper, but has a rather coarser flavour than the Golding hops. The cone is large, square in section and pointed. The petals are thick and those at the base of the cone are dark green. It is very widely grown in Kent, Sussex, Worcester and Hereford and particularly suited to the heavier land. Some of the strains developed by individual growers stand out on account of their high quality, and it appears to be particularly well suited by the Worcester and Hereford soil, where it grows without any rankness of flavour.

A few other varieties are grown in England, but only to a very limited extent. The Tolhurst is the best known of these and gave its name to a class of inferior quality in the Hop Control grouping. It is similar to the older Prolifics, which have practically ceased to exist. It is a very heavy cropper and was introduced after the War, when it was desired rapidly to plant up new gardens, but it is now grown only to a very limited extent, on account of

its poor aroma and low preservative power. The Colegate, raised from a wild hop by Mr. D. Colegate of Chevening in 1805, is a small narrow hop, square in section, with thin pale petals and a coarse flavour. It was the latest hop to ripen, frequently not being ready to pick until October, for which reason it was expensive to grow and has been practically abandoned. Really ripe samples were, however, of quite good quality.

It is difficult in many cases to determine the variety of packed hops, though Tolhursts can almost always be distinguished by their lack of hop flavour and frequently objectionable aroma. Usually they were picked first and often under-ripe, consequently many samples had a peculiar greenish complexion. Fuggle's can be distinguished from Goldings by their more pointed shape, lack of the yellow colour at the tips of the petals and coarser aroma. It is a simpler matter to determine the variety of growing hops, from the shape of the leaves, colour of the bine, style of growth and more particularly from the shape of the cone and its aroma. The longer cones with flattened sides and the greener colour of the basal bracts distinguish the Fuggle's from Goldings.

(292) Breeding New Varieties of Hops.

Methods of hybridisation have been extensively used for the production of new varieties of hops, particularly by E. S. Salmon at the South-Eastern Agricultural College, Wye, Kent. The objects have been to combine the desirable properties of selected parents in one and the same variety, the high preservative value of Oregon Clusters with the flavour of English hops, for example. Very considerable success has attended the work carried on since 1907 and many seedlings have consistently produced large crops of hops with high preservative values. Most of the new hybrids are still known only by numbers but a few have received names as they were recommended for general cultivation. Of these Brewer's Favourite and Brewer's Gold were the first,¹ to be followed by Fill-pocket and Quality Hop.² Brewer's Gold was derived from a wild Manitoba hop, crossed with an English male, and has the highest preservative value ever found in hops, 120 to 140 on moisture-free hops by gravimetric analysis. It has a very rank aroma and could not be used alone in the copper, but brewing trials have shown that it is useful in blends and even as dry hops for filtered beers. Cut samples have an exceptionally rich and stout appearance. Brewer's Favourite and Fill-pocket are both second crosses of an Oregon Cluster with English males. They have been successfully used in the copper and have high preservative values. Quality Hop is the result of a third cross with an English male hop and is exceptionally rich in resins.

(293) English Hop-growing Districts.

Hops are grown in eight English counties, Kent, Surrey, Sussex, Hampshire, Hereford, Worcester, Berkshire and Shropshire. Kent has a greater output than the others put together, 150,800 cwt. of a total output of 252,000 cwt. in 1936, from an area of 10,106 acres out of 18,317. In 1936, Hereford grew 45,000 cwt., Worcester 22,300, and Sussex 24,200 cwt. Three hop-growing areas are distinguished in Kent, differing in soil and consequently in the types of hops generally grown. East Kent, with a light loam, frequently over brick-earth. Mid-Kent, with loam over ragstone and the Weald, with loam over a clay subsoil. The soil in Worcester and Hereford is generally heavier and deeper and the crops there usually about 2 cwt. per acre less than the average for Kent. The hops of these two areas are distinctive in aroma, some brewers prefer one and some the other. Methods of drying are more advanced in the Hereford and Worcester district, in that a greater percentage of the hops, some 80%, is dried by pure air systems. This is no doubt largely a question of the expense of replacing plant in the older gardens of the south, where great changes have been made during recent years. The Sussex district is a continuation of the Weald of Kent, while the district centred round Farnham is of considerably smaller area but has a very high reputation for quality. Hops are only grown in Berkshire and Shropshire in isolated farms. Each of these districts is associated with one or more varieties, to which its soil and climate are particularly adapted, and it is usual to refer to both district and variety when describing hops. These are indicated in Table 108.

TABLE 108.—DISTRIBUTION OF HOPS IN ENGLAND

District	Chief varieties
East Kent (Canterbury, Faversham)	Goldings and Bramling, Cobb and Tutsham.
Mid-Kent (Valley of Medway, Maidstone to Tonbridge)	Fuggle's, Bramling, Tutsham, Cobb, Goldings, Tolhurst.
Weald of Kent (Tonbridge to Sussex)	Fuggle's.
Sussex	Fuggle's.
Hampshire, Surrey	Fuggle's, Farnham Whitebine.
Hereford and Worcester, Valleys of the Teme and Frome	Mathon, Bramling, Fuggle's.
Berkshire and Shropshire	Fuggle's and Goldings.

(294) German Hops.

The most important hop-growing districts in Germany are Hallertau, Spalt and Hersbruck in Bavaria, Tett nang or "Ober-

land" and the "Unterland" around Rottenburg, Herrenberg and Weilderstadt in Württemberg. Each district is characterised by a predominant variety, suited to the local conditions and derived by selection from older kinds, though early and late strains are cultivated in many districts. It is consequently possible to designate the chief varieties by the name of the locality in which they were grown and to expect definite characteristics in each, although mixture of varieties inevitably occurs to a certain extent.

The Hallertau is the predominant German variety, since the Hallertau, north of Munich, is by far the largest hop-growing district. It is well suited to the country and is consequently gaining ground in such districts as Kinding and Aischgrund, where special varieties were formerly grown. It is a mid-season hop of high preservative power and strong flavour, but the finer strains are very susceptible to Downy mildew.

Spalt is a mid-season hop of more delicate and finer flavour than the Hallertau, named after a district to the south of Nürnberg. Hersbruck, a district lying to the south-west of Nürnberg, is not so well suited as Hallertau and Spalt to the growth of the finest hops. The typical Hersbruck hop is late season, but some early hops are also grown. The Striesslspalt or late Alsace hop is still grown to a considerable extent in the Hersbruck and also in the Württemberg Unterland, despite its indifferent quality. Its lupulin content is low but it has a very distinctive green colour which is attractive to some brewers.

Among Württemberg hops, the Tettngang, grown in a very favourable district close to Lake Constance, is the first to come on the market. It has a fine, delicate aroma and is largely used for high quality lager beers. The Rottenburg, a late hop largely grown in the Württemberg Unterland, is a stronger hop, without the delicate aroma of the Oberland Tettngang.

Hop production in Germany is still largely in the hands of small growers and the hops are grown in many places on poles, but a simple wire and string system is generally used in the Hallertau and Spalt districts. The hops grow to about 20 feet almost vertically on the strings or poles. Usually about 1,600 hills are planted to the acre, from each of which two vines are grown up each string. The total crop in 1935 was about 200,000 cwt. on 22,000 acres, of which Hallertau grew about 135,000 cwt. on 12,500 acres.

(295) Czechoslovakian Hops.

The most important district, famous for the quality of its hops, is that of Zatec or Saaz in Bohemia, about 50 miles to the North-West of Prague. 75% of the Czechoslovakian hops are

grown in the Saaz area. Roudnice and Ustek or Auscha are also well-known districts, while there are smaller hop areas in Dauba and Tosica in Moravia. The hops are cultivated in a similar manner to that adopted in Bavaria. The outstanding variety, an early red bine, is not a very heavy cropper but produces hops of the choicest quality and most sought-after of all for pale lager beers. According to Salmon, it is related to the Fuggle's variety, like which it shows considerable resistance to Downy mildew, but it has been attacked by this fungus since 1932. The total acreage in 1935 was about 28,000, with a crop of about 150,000 cwt.

(296) Yugoslavian and Polish Hops.

The climate in the districts of Slovenia and Wojwodina and in the north-east of the country is well adapted to the cultivation of hops. The local requirements are small and consequently a large proportion of the crop is available for export. The Styrians are of high quality, though very susceptible to Downy mildew. Four principal varieties are distinguished, (1) an early red bine hop of Czechoslovakian origin, (2) a mid-season, green bine hop of English origin and referred to as a Golding, though probably derived from the Fuggle, (3) a high quality late hop derived from Czechoslovakia and known as the Styrian and (4) a late green bine from Württemberg. The crop amounted to about 74,000 cwt. from 8,600 acres in 1935.

The position in Poland in regard to export is similar to that in Yugoslavia. The conditions in some districts around Volhynia and Lublin are suited to the production of choice hops and fine samples are frequently exported. A smaller growth comes from Nowy Tomsyl. The identity and quality of Yugoslavian and Polish hops has suffered through the misleading trade custom of selling growths from these countries and others as Saaz sets. This name gave no indication of origin and covered a wide range of quality. Its use is now restricted by the advance of marketing organisations in the two countries named and recognition of the fact that exportation of sets from Saaz is prohibited. About 42,000 cwt. were grown in 1935 on 7,600 acres.

(297) French and Belgian Hops.

The most important hop-growing district in France is in Alsace, though hops are also grown in Burgundy, Lorraine and in Flanders, adjacent to the Belgian hop fields. The quality is not generally regarded as high, though good hops are produced in Alsace, where a variety known as Alsace and another derived

from Spalt are grown. The 1935 crop amounted to about 46,000 cwt. from 5,000 acres.

Poperinghe is the centre of one of the oldest hop-growing districts, but the hops of the country in general are not of a high order and Czechoslovakian and German hops are imported in large quantity for the lager beers. Recently the cultivation of the male hop has been prohibited and efforts are being made by selection of improved varieties, such as the Buvrinnes, to improve the general standard of quality. The crop in 1935 was about 25,000 cwt. from 2,000 acres.

Taking the Continental hops as a whole and comparing them with English hops it may be said that they have a distinctive flavour that limits their use in English beers, but that the greater strength of some of the better qualities has led to considerable importations of Hallertau, Saaz, Styrian and Polish hops for use in blends with English and, in some cases, the compact, unbroken, seedless cones and flavour have decided their use for dry hopping. For lager beers, on the contrary, these hops take the premier place, Hallertaus are typical of hops used in beers for which a strong hop is required, while Saaz, Tettnang and Spalt are preferred when greater delicacy of flavour is of importance. The seeds of the English hops place them in an unfavourable position with lager brewers who demand a seedless hop.

(298) American Hops.

Hop cultivation is most extensively developed in the United States on the Pacific Coast, though small quantities are still grown in New York State. The most important centre is the Willamette Valley in the north-east of Oregon. In California the principal centres of production are the Sonoma, Russian River and Sacramento districts, the quality of the hops usually being in that order. The climate is very favourable for hops, with summer temperatures similar to those of Bohemia and abundant early rainfall, though irrigation is practised in some districts of California in the dry weather. Little manuring is required and the fertility is such that a crop may be picked in the first season in California and in the second in Oregon. Considerable quantities of similar hops are also grown in Western Washington and the Yakima Valley. Drying is carried out by hot air, forced from an enclosed furnace adjoining the large kilns. The most important variety grown in the Western States is the Oregon or Late Cluster which, according to Salmon, possibly originated as a hybrid between an imported English hop and the wild American hop. It is particularly rich in lupulin, but has a strong flavour resembling blackcurrants and gives

a characteristic strong bitter flavour to beer. An earlier maturing selection of this hop, called the Early Cluster, and Fuggle's hops imported from England are also grown to a smaller extent. Hop growing was formerly a flourishing industry in New York State, extending up to Canada, but was practically wiped out about 1910 by a disease which, it has been suggested, bore a resemblance to, if not identical with, Downy mildew.

The very strong blackcurrant flavour, frequently referred to as "tom cat," of some of the Cluster hops of the Pacific slopes greatly limits their use but their high preservative power makes them valuable in a blend with English hops. A higher rate can be used with gypseous waters, with which the characteristic flavour does not develop to the same extent as with carbonate waters. Hops of a less pronounced flavour are increasing in quantity as a result of selection. The total crop in 1935 amounted to about 345,000 cwt. from 39,000 acres.

(299) British Columbian Hops.

The Western American hop-growing area extends into British Columbia, where a considerable quantity is grown in the Fraser River Valley around Sardis and on the Sumas Prairie. In this State there has been an important cultivation of Fuggle's and Golding sets, imported from Kent originally by Lord Aberdeen in the middle of last century, rapidly supplanting the Cluster variety formerly generally grown. Hops from the English sets retain their original flavour characteristics, though modified to a slight extent by conditions of growth, climate and soil. A more or less pronounced American flavour in hops from gardens originally planted with Fuggle's is due to replacement of dead hills by Cluster sets. The preservative value of the British Columbian hops is high, resembling that of Oregons. About 16,000 cwt. were grown in Canada, in 1935, on about 1,100 acres.

(300) Australian and New Zealand Hops.

The most important centre in Australasia is in the south of Tasmania, where a limited quantity of hops is grown. These have been derived from English and Californian sets. A small quantity of Golden Clusters is also grown in the Owens River Valley in Victoria and a rather larger area is under hop cultivation in New Zealand, where the sets were obtained from America and England. About 30,000 cwt. were grown on about 1,800 acres in 1935.

BREWING VALUE OF HOPS

(301) Physical Examination of Hops.

The brewing value of hops depends essentially on their aroma and preservative power, that is mainly on the quantity and condition of certain constituents of the oils and resins. They are usually judged and valued by hand examination of cube-shaped samples of about 8-inch side, cut from the pockets, but many brewers now rely on analysis for the final decision on preservative value. A very reliable estimate of brewing value can, however, be obtained from hand examination of the sample, since the cut surfaces pass through many cones and reveal the quantity of lupulin and seeds. The lustre and colour is shown by parting the sample in the direction of the grain, while the aroma and lupulin are judged by rubbing a portion down in the palms of the hands. The points taken into consideration include :

(1) The "spring" of the sample, as judged by pressing it with the hand. Lack of elasticity denotes excessive moisture in hops which are "out of condition."

(2) The "rub," determined by rubbing down a small handful, reveals the quantity of resins by the amount of sticky material left on the hands and also discriminates between the silkiness of high quality hops and the rougher texture of coarser hops.

(3) Aroma or "flavour" is also judged from the rubbed-down sample and is the surest guide to the general quality or utility of the hops. It must be realised that different varieties have varying aromas and the most suitable hop for one purpose is not always the best for another. The delicacy of Golding or Saaz hops differentiates them from the stronger flavoured Fuggle's or Hallertau, while the characteristic aroma of the Oregon Clusters and other American hops places these in quite another category, but there are variations in every variety which determine selection or rejection for the purpose intended. Aroma is a difficult matter to assess, as personal preferences differ and lead to the selection of different varieties or of hops from different localities. These preferences are based on experience that one type or another suits the particular brewery best.

(4) Foreign odours or aromas that are not typical of a good sample of the type under consideration are quite another matter. The sample would be penalised or rejected if any were detected. The aroma depends on the condition of the essential oils, which are progressively oxidised or polymerised as the hops get older, with corresponding change in its character. Among foreign odours are those due to disease and defects in management. Any trace of the odours of butyric or valeric acid or of mould would cause

rejection. Faulty kiln treatment may be detected by an odour reminiscent of hay, if the hops are under-cured, or of malt, if unduly high temperatures were used. The effects of "reek" or of smoke may also be found.

(5) Colour and general appearance. The degree of maturity reached by the hops is a most important factor in their quality. Fully ripe hops are advisable in most cases, both on account of the flavour they impart to the beer and because of their greater preservative value. There are, however, some brewers who prefer green hops, believing that the varieties they use have the most delicate flavour just before they take on the primrose yellow of maturity and that they give paler beers. When very ripe, the cones become reddish-brown and care is required to distinguish between the brown colour due to disease or damage from wind or weather and that of fully ripe hops. In wet years the green of under-maturity becomes all too frequent, on account of the growers' fear of loss if they fail to take advantage of a favourable but too early opportunity for picking. The colour is in some cases a guide to the variety of the hops. Goldings can be distinguished by a typical yellow on the tips of the petals and Tolhursts have, in many cases, a characteristic green appearance.

High quality hops are distinguished by a silk-like gloss. A dull appearance suggests that the hops have been subjected to "heat" at some time. This may occur if they are kept too long in the poke before kilning or through bad management on the kiln, with moisture from the lower layers of the bed of hops condensing on those above and, in bad cases, producing reeked hops. A brownish-yellow in the middle of the cones indicates insufficient drying of the strigs, through too rapid kilning. Heating in the pocket, due to packing when too moist, is revealed by brown discoloration and, in bad cases, the hops go black in parts of the pocket, until the whole is ruined.

Minor faults due to wind and weather may not affect the brewing value of hops, so that care should be taken to distinguish the brown petals or tips caused by wind damage and the reddish-brown spots due to hail from the discoloration of mould or Downy mildew. Bad cases of fungoid diseases can be detected by the deformed and rotted cones they cause and the blackish-brown colour.

(6) Size of cones and freedom from breakage. Well-formed stout cones are evidence of well-grown hops, but size is frequently associated with coarser hops and it is generally the medium-sized, compact types that are preferred. Whole cones are particularly required for dry hopping, but this must be associated with good aroma.

(7) Extraneous matter. Careless picking or packing is revealed by the presence of leaves, strigs and other extraneous matter, which may considerably lower the value of the hops.

(8) An excessive quantity of seeds is always a disadvantage and there should be none in most Continental hops.

Point systems for valuation of hops have received little favour in this country, but they can be applied successfully in competitions and the like by allotting a maximum number of marks for perfection, with deductions according to defects noted. Thus the Society for Hop Research in Freising, Bavaria, adopted the following :

Picking	1 to 4 points
Moisture and condition	1 to 5 „
Colour and gloss	1 to 10 „
Cone shape	1 to 15 „
Lupulin	1 to 15 „
Aroma	1 to 15 „

The maximum number of points for a high quality hop is thus 64, from which 1 to 15 points are to be deducted for disease and 0 to 15 for faulty management. Good quality hops should reach 50 points, while 40 to 50 indicates second quality. The presence of stalks and leaves is used as the guide for picking. Moisture is judged in the hand only. It should be between 10 and 11%. The stalks and strigs bend instead of breaking if excess is present.

(302) Flavouring Properties of Hops.

It is difficult to assess the relative importance of the two factors, preservative power and flavour, in their relation with the brewing value of hops. They are both so intimately connected with the resin content of the hops, that it is usually safe to consider flavour first, with the assurance that a pleasant bitterness will be associated with adequate stability in the beer. The resinous bitter substances are mainly of colloidal character and the bitterness of beer depends on the degree of their dispersion, being more intense as this is greater, on account of increased surface effects on the sensory nerves. Alkalis tend to increase the dispersion of colloidal substances and also form bitter compounds with the resin acids, explaining the varying effects of different liquors on the flavour of beer. Carbonate liquors, by increasing the p_H value of wort, hasten the change to resinous products and also limit removal of the latter from wort by preventing the formation of a bulky coagulum. With a bad break, the minute protein particles carrying adsorbed resins pass to the fermenting vessels, where some of the resins are again dispersed in the wort, increasing its bitterness.

With increasing acidity during fermentation, the degree of dispersion of the resins is reduced and their precipitation on the yeast or surfaces of the fermenting vessel thereby assisted. A striking connection between attenuation and bitterness has been noted in some comparative brews with different hops by Tombeur and De Clerck.³ The least bitter beers had a thin flavour, although least attenuated, as hops contribute to the fulness of beer as well as to its bitterness. The association of the resins with beer flavour is thus complicated by variations in the colloidal conditions existing in the wort, marked by differences in the break, amount of cooler sludge, fermentations and yeast heads.

The α -fraction of the soft resins conveys much more bitterness to wort than the β -fraction. Walker and Hastings⁴ described the taste given by the latter as slight and astringent, rather than bitter, becoming decidedly unpleasant after boiling for 3 hours. The α -fraction gave rise to an intensely bitter flavour when first added to wort, due probably to colloidal dispersion of the humulon in a chemically unchanged condition. The time required to reach the maximum bitterness was found to depend on the concentration of the resin and the intensity of boiling. After the maximum was reached, a gradual decrease was noted, a nauseous flavour, similar to that produced by long boiling of the β -fraction, becoming noticeable. It was found that the α -fraction gave no aroma but that the β -resins were definitely pleasant in this respect. Lupulon itself contributes little if anything to the bitter flavour of hops, but humulon gives a very bitter flavour and, on account of its acidic character, forms salts with alkalis which are more readily soluble and more intensely bitter than the acid itself, accounting partly for the effect of alkaline liquors on beer flavour.

Wöllmer's brewing value of $\alpha + \frac{\beta}{9}$, which, it was claimed, gave the relation between bitterness and resin content, is useful for calculating hop rates on the basis of resin analyses in the case of hops of the same type, but it does not hold when comparing hops of different variety and character. There appear to be varietal differences in flavour, quite apart from the effects of the humulon and β -resins. Thus, proportionally more of delicate flavoured hops than analysis suggests is required to give equal bitterness with other varieties characterised by stronger or harsher flavour. Schmidt, Winge and Jensen⁵ found that the α -, β - and hard resins had relative "bitterness values" of 10 : 7 : 4, when boiled in wort. They claimed that determination of the total resins of an ether extract of hops, previously dried *in vacuo* at 85° C., by titration with 0.05N alcoholic KOH gave a good indication of their bitterness. (Section 274.)

Nothing but experience can give the ability to pick out the most suitable hops for different beers. The choice may also vary in different breweries, depending partly on the liquor and partly on the method of boiling. Longer boil or pressure boiling extracts more of the resins and causes greater changes, which must be allowed for in the type or quantity of hops used. Similar differences in flavour result from the use of new or older hops. It is not usual to employ the current season's hops until about 3 months after harvest in order to avoid excessive bitterness and then they are blended in gradually increasing proportions with the last season's hops, in order to maintain a constant bitterness. The rate is also suitably adjusted as the year goes on, particularly as greater preservative power is required in the summer, when the antiseptic value has become smaller.

Pacific Coast hops can rarely be used immediately after arrival in England, unless the liquor is very gypseous. In the majority of cases they are to be preferred as yearlings, when they give a milder flavour with adequate preservative power. The character of Continental hops can generally be detected, when used in the copper, while brewers in different parts of England have preferences either for Worcester or Kent hops.

Filtration of the beer has a most marked effect on the hop flavour and it is advisable to use a higher hop rate with filtered beer than with similar qualities which are not filtered. In many instances a strongly flavoured Pacific Coast or Continental hop can be used in filtered beer with advantage and in much higher proportion than would be possible with the same beer unfiltered. This point must be seriously considered when selecting dry hops for use in tanks of chilled and filtered beer. There is even a wide range of preference in respect of dry hops for use in cask. Most brewers prefer the marked but delicate bitter produced by Goldings in comparison with the generally somewhat rougher flavour given by Fuggle's hops, but a choice Fuggle's frequently gives very good results. Others find that Saaz or even the stronger flavoured Hallertau hops give them the best results in cask, while Styrians are sometimes selected for that purpose.

In all cases care must be taken to reject hops which are obviously damaged by fungoid diseases or which have been depreciated by bad management in drying or storage. Defects in flavour can be traced to any of these causes. Downy mildew may make itself very noticeable if the hops are badly infected. Over-drying takes away the pleasant flavour and under-drying results in lack of flavour. Reek on the kiln may be conveyed to the beer, while hops stored with an excessive moisture content may develop mouldy flavours or traces of valeric acid, even if the damage is

far short of the blackening sometimes seen in the interior of a pocket of imperfectly dried hops.

(303) Relative Preservative Values of Different Varieties of Hops.

It is not possible to give strictly characteristic analyses of different varieties of hops, owing to the wide variations produced by seasonal and local conditions, but an approximate idea of varietal differences in preservative value can be obtained by comparing a number of varieties grown year after year in the same garden. This method of comparison has the drawback that some of the varieties would be better suited by local conditions than others and might be placed higher in the list than their general market quality warranted, while others would not take the position they generally attain when grown in the district where they develop to the best advantage.

TABLE 109.—ANALYSES OF HOPS GROWN AT EAST MALLING IN 1932 AND 1931
(VALUES EXPRESSED ON MOISTURE-FREE HOPS)

Variety of Hops	Resins per cent.			Preserva- tive value
	α	β	Hard	$10\left(\alpha + \frac{\beta}{3}\right)$
1932				
C9a (Brewer's Gold)	10.42	13.37	3.02	148.8
OP 21 (Brewer's Favourite) ..	6.80	11.96	1.21	107.9
Mathon	6.58	9.47	1.14	97.4
Petham Golding	6.36	9.96	0.39	96.8
Canterbury Golding	5.95	10.74	0.79	95.3
Tutsham	6.04	9.30	1.11	91.4
Fuggle's	5.86	9.47	0.56	90.2
Bramling	6.18	8.15	0.76	89.0
Rodmersham	5.63	8.90	0.44	86.0
1931				
C9a (Brewer's Gold)	6.67	10.04	—	100.2
OP 21 (Brewer's Favourite) ..	5.39	9.00	—	83.9
Canterbury Golding	5.05	7.82	—	76.6
Mathon	4.41	7.01	—	67.4
Fuggle's	4.25	7.43	—	67.3
Petham	4.20	7.40	—	66.7
Bramling	3.36	9.10	—	63.9
Rodmersham	3.97	6.33	—	60.8
Tutsham	3.51	7.30	—	59.4

The analyses by Ford and Tait's method given in Table 109 (E. S. Salmon⁵) represent hops grown at the East Malling Research

Station, Kent, in 1932, which was a very favourable year for hops, and in 1931, when the weather conditions were adverse and the preservative values of the hops were reduced by about 25%, a difference which by no means over-states the average difference in preservative values of the English crops of 1932 and 1931. Despite the varying response of different varieties to weather conditions, it will be noticed that the hops represented at East Malling came approximately in the same order of preservative value in both years. Individual growths of any of the varieties, under exceptionally favourable soil and climatic conditions, helped by good management, or suffering under the reverse conditions, may have differed widely from the values given in either year. The sample of the prize growth of Fuggle's in 1932 had, for example, a preservative value of 107·7 on moisture-free hops.

The preservative values of high quality Pacific Coast hops and of the choicer Continental seedless hops are usually higher than those of English, but similar variations occur, though these may be less marked on account of more constant climatic conditions. Typical analyses representing choice hops from various countries are given in Table 110.

TABLE 110.—ANALYSES OF HIGH QUALITY FOREIGN HOPS
(VALUES ON MOISTURE-FREE HOPS)

Origin	α	β	Hard	$10 \left(\alpha + \frac{\beta}{3} \right)$
Sonomas	8·46	10·91	2·43	121·0
Oregon Clusters	7·47	11·86	1·20	113·6
„ Fuggle	7·05	8·70	1·80	99·5
British Columbian Clusters	7·05	10·50	1·58	105·5
„ „ Fuggle	6·50	10·06	2·00	98·5
Hallertau	7·50	9·60	1·80	107·0
Saaz	6·88	9·80	1·70	101·5
Styrian	6·55	10·50	2·20	100·0

(304) Preservative Value of Different Grades of Hops.

Round figures for the relative preservative values of hops of different grades are given in Table 111. Full allowance must be made from these figures for seasonal variations, on account of which a particular growth with a preservative value of 90 in one year might only attain 70 to 80 after an inclement season, when the values for other hops in the same district would probably vary proportionally.

TABLE 111.—RELATIVE PRESERVATIVE VALUES OF VARIOUS GRADES OF HOPS
(ANALYSES OF HOPS WITH 10% OF MOISTURE)

Grade of Hops	P.V. $10 \left(\alpha + \frac{\beta}{3} \right)$
Low P.V. "olds" and "old olds"	20-50
Low grade Prolific hops	50-60
Moderate value for English hops	60-70
Good values for English hops	70-80
High P.V. for English hops, good Continental and American hops	80-90
Very high P.V. rarely reached by English hops. High-class American and Continental hops	90-100
Occasionally reached by American hops	110

(305) Preservative Substances in Wort and Beer.

The Log phase method of analysis devised by Walker and Hastings has made it possible to estimate the antiseptic value of the hop extractives in wort and beer. Results of such analyses have shown good correspondence with the preservative value of the hops, when the brewing methods have been standardised. Examples to illustrate this are given in Table 112. They refer to experimental boils which showed that the wort attained its maximum antiseptic content after 90 minutes' boiling as a result of the balance between the gradual solution or dispersion of the resins and their destruction. The figures represent the relative antiseptic values of unit volumes of the wort at different times during boiling, the highest value found with hop A being taken as 100. The relative preservative values of the hops used were determined by gravimetric analysis and represented by $10 \left(\alpha + \frac{\beta}{3} \right)$.

Hop B was actually a mixture of two hops, the preservative value being calculated from individual analyses and the proportions used. The approximately definite relation between the antiseptic content of the worts and the relative preservative value of the hops give further confirmation of the utility of hop analyses.

TABLE 112.—PRESERVATIVE VALUES OF HOPS AND WORTS

	Hop A	Hop B
Relative P.V. of hops	83.7	49.1
" " of wort boiled 60 minutes ..	91	62
" " " " 90 " ..	100	70
" " " " 100 " ..	88	61

The method has been applied to determine the loss of antiseptic material through the various stages of brewing, with results generalised by Walker ⁶ in Fig. 59. Further details of the changes in the resins during brewing are given in later chapters.

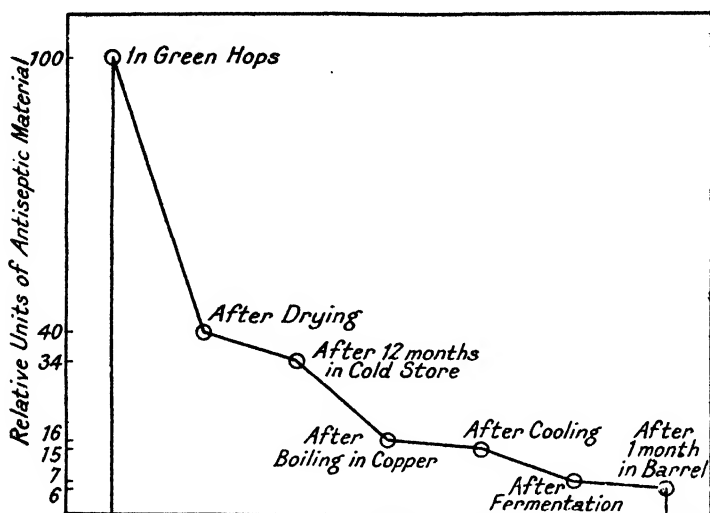


FIG. 59

DIAGRAM SHOWING APPROXIMATE LOSS OF ANTISEPTIC MATERIAL DURING DRYING, STORAGE, AND IN EACH STAGE OF BREWING

(306) Preservative Value of Dry Hops.

The solubility of the antiseptic resin constituents of hops or their dispersal in beer is slow and several weeks are required to obtain the full preservative value from dry hops. The same applies to the aroma derived from the essential oils. The figures in Table 113 show the increase in the antiseptic content of beer produced by the addition of 6 oz. per barrel of dry hops. They were derived from large scale brewing trials with the hops referred to in Table 113. The preservative value of the beer in which hop A was used is taken as 100, the other values are in relation to this.

TABLE 113.—EFFECT OF DRY HOPS ON THE ANTISEPTIC CONTENT OF BEER
(RELATIVE PRESERVATIVE VALUES)

		3 weeks	7 weeks	11 weeks
Beer brewed with hop A ..	No dry hops	100	100	100
	Dry hop A	109	110	107
Beer brewed with hop B ..	No dry hops	75	70	70
	Dry hop A	86	88	96
	Dry hop B	85	84	90

(307) Contamination of Hops.

Hops may be contaminated with sulphur, copper or arsenic from the sprays or fuel used. Sulphur in excessive quantity is liable to lead to stench in the beer and the presence of SO_2 in greater quantity than usual may, by adding to that in the beer, lead to excess over the permitted quantity of 70 parts per million. Sulphur may be detected by production of sulphuretted hydrogen, when a current of hydrogen is passed through a decoction of the hops, and estimated by formation of lead sulphide. Sulphur dioxide can be determined in the usual manner and should not exceed 2,500 parts per million. The limit of 1/100 grain per pound is usually accepted for arsenious oxide, in line with foods, though it would obviously require much greater quantities to give 1/100 grain per gallon in the beer. This limit is rarely exceeded in air-dried hops and only if insufficient care is taken in selection of coal and sulphur in hops dried on open fires. There should be no fear of contamination with copper if the Bordeaux mixture sprays are properly applied. 200 parts per million of copper is rarely exceeded in hops. This is equivalent to 1.4 grain per pound of the hops of which Heron⁷ found that $\frac{3}{4}$ may be dissolved in the wort, in which about 0.05 grain per gallon would be found if the hops were used at the rate of 2 lb. per barrel. This is approximately the quantity found in beers brewed in copper vessels and below that required to produce haze. The greater proportion of the copper dissolved is, however, removed by the yeast during fermentation. 200 parts per million of copper in hops may be considered as a permissible limit.

SUMMARY**(308) Selection of Hops.**

The selection of hops for brewing any particular type of beer must depend, in the first place, on a thorough physical examination. In no other way is it possible to eliminate those in which the aroma has been detrimentally affected by disease or bad management and to select those best suited to the purpose in view. Different varieties have characteristic aromas, strength or delicacy of flavour, which make them particularly suitable for various uses or types of beer. Thus, a stronger flavoured hop is more generally useful for copper than dry hopping purposes, in which delicacy of aroma and compactness of cone are the chief desiderata. A strongly flavoured hop is, however, useful for dry hopping filtered beers. Copper requirements also vary greatly according to the hop character of the beer. It is generally possible to use a stronger hop with mild ales and dark beers in which the hop rate is low, than in pale

bitter beers, for which a higher hop rate, combined with delicacy, is required. It is not generally possible to increase the hop rate with the stronger flavoured hops in order to increase the bitterness, as it usually gives rise to an objectionable rankness. The proportion of the stronger hops which can be used without detriment to flavour also depends, to a great extent, on the nature of the brewing liquor. A much higher proportion can be used with gypseous liquors than with carbonate waters, which increase the rankness.

Strength of flavour or delicacy is associated with certain varieties of hops and it is always necessary to take note of the type of hop used. The differences between the flavours of the Oregon Cluster of America, most Continental and English hops are very marked and in each group there are variations due to race. Thus in England the Goldings are characterised by greater delicacy than the Fuggle's. Varietal differences are particularly marked among Continental hops, the Saaz and Early Tettnang are prized on account of their delicacy, while the Hallertau hops are known for their strength of flavour. These characteristic varietal differences are modified by growth in different localities and also by management during growth and curing. Thus the Kent and Worcester hops have characteristics which recommend one or the other to different brewers. It is possible by analysis to obtain a fair comparison of the bitterness which hops of the same type will give, but the comparison fails with hops which have markedly different varietal character. The bitterness is mainly due to the humulon and its primary products of change and the comparison between similar hops is given by $\alpha + \frac{\beta}{9}$. The original strong flavour of Pacific Coast hops becomes modified by storage, so that they are frequently used with advantage as yearlings.

Sufficient evidence has been obtained to warrant the use of gravimetric and biological methods of analysis as an indication of the relative preservative value of hops. The final selection from a number of hops, which have been passed as suitable in regard to flavour and free from obvious defects, should consequently be based on analyses. For this purpose determination of the percentages of the α -fraction, or humulon, and β -resins is satisfactory, the comparison being based on the figure for relative preservative value obtained from the expression $10 \left(\alpha + \frac{\beta}{8} \right)$.

Values obtained in this way vary considerably from year to year with hops of the same growth, so that it may be necessary to vary the standard on which selection is made in accordance with the weather of the season. Analyses show that hops depreciate pro-

gressively in preservative value during storage. This depends largely on resinification of the humulon, shown by reduction in the percentage of α -resins, and results in a comparable reduction of bitterness. It is in consequence necessary to increase the hop rate as the season advances, particularly as greater preservative power is required in the summer months.

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WATER

CHAPTER XVIII

BREWING WATERS

PURITY OF BREWING LIQUORS

(309) Water Supplies.

The fact that certain localities are renowned for beers of a particular type, apparently impossible to reproduce elsewhere, is usually attributed to the composition of the water supplies, but should not be taken as proof that the character of the beer is in all cases dependent on the brewing liquor. So many other factors are operative that it is almost impossible to produce an exactly similar beer in different breweries. Some of these factors are known and reproducible but others are only suspected or quite unrecognised. The plant may apparently be duplicated, the same materials used, the same liquor and yeast employed and the human element eliminated as far as possible by joint control and, yet, the beer from the two breweries will probably have more or less distinct characteristics. In some cases these may be traced to specific micro-organisms which gained a lodgment in the brewery, in others they appear to be due to apparently insignificant variations in plant or procedure. Despite the large number of factors which combine to stamp the product of each brewery with a distinct individuality, there is no doubt that the influence of the liquor is very definite and can to some extent be foreseen and controlled. Consequently the water supply of a brewery is of primary importance and a first consideration when deciding on a new site.

Preoccupation is not limited to a plentiful supply of organically pure water of suitable composition for brewing. Full consideration must also be given to such ancillary requirements as cooling, steam raising, washing plant, casks, etc. The amount of water required for these purposes is so great that 10 or, in hot countries, as much as 15 barrels of water for each barrel brewed are necessary. So much of this is required for cooling, that a supply at a low temperature throughout the year is greatly to be desired. In view of this, it is necessary to decide whether first consideration should be given to brewing liquor, for which a hard water is often preferred, or to steam raising, bottle washing and other purposes for which a

soft water is desirable. In many cases it is impossible to find water suitable for both purposes and difficulty in finding what is held to be the ideal liquor for the proposed type of beer, together with the greater cost of softening as compared with hardening, will generally turn the scale in favour of a soft water, which could be treated for brewing if thought desirable. A large proportion of the public water supplies are derived from rivers and lakes and in many cases these are suitable for brewing or can be treated in a comparatively simple manner, while their purity is generally above suspicion. The cost of such water, however, usually makes it preferable to depend on wells and bores, unless the position of the brewery and the unsuitability of the water obtainable renders this course undesirable. In particular, very hard waters containing a high proportion of carbonates, waters with a high content of common salt or other sodium salts, containing iron or having an objectionable odour and turbid waters are to be avoided.

(310) Substances dissolved in Water.

All natural water supplies may be looked upon as dilute solutions of salts, in which small quantities of gases and organic matter are also dissolved. This even applies to rain water, which almost always contains appreciable quantities of ammonium and other salts derived from the atmosphere. As rain water runs over the surface or through fissures in the more impervious rocks or passes through the shallow covering of soil and vegetation, ultimately to collect in streams, lakes and reservoirs, it gains further small quantities of mineral and organic matter and carries them forward in solution and suspension. Whenever the nature of the rocks permits, the water percolates through them, until prevented by occurrence of impervious strata. In its course it is subjected to processes of filtration and purification, so that deep well waters are usually practically free from organic matter. Shallow well waters may also be organically pure, but the liability to contamination from insufficiently filtered effluents from farmlands or sewage must not be overlooked.

In addition to the purification and oxidation of organic matter, which occur during the passage of water through the rocks, there are constant additions to the amount of mineral matter dissolved, so that well waters are nearly always hard. The nature of the substances taken into solution and their quantity vary widely, according to the composition of the strata through which the water flows. As these consist for the most part of sands and clays, a small quantity of silica and alumina is always taken up and very

often a little iron oxide, but the saline constituents of main interest in brewing are derived from the more soluble minerals, consisting of calcium and magnesium carbonates and sulphates with various salts of sodium and potassium. The solution of chalk and limestone depends on the presence of carbon dioxide in the water and calcium bicarbonate is the most abundant mineral constituent of waters, accompanied in some places by considerable quantities of magnesium carbonate, gypsum, magnesium sulphate, sodium sulphate and chloride.

As a result of the presence of these various substances in the rocks of the catchment areas, the waters are spoken of as chalk, carbonate, magnesian, gypseous, saline waters, etc., to denote the nature of the predominant mineral constituent. The total quantity dissolved rarely exceeds 0.2% and is more commonly less than 0.05%. In such dilute solutions the dissolved salts are believed to be almost completely dissociated into ions, so that no, or very little, calcium bicarbonate, gypsum, sodium chloride or other salt actually exists in the water. The practical study of brewing liquors consequently resolves itself into considerations bearing (1) on their organic and bacteriological purity and (2) on the effect of the ions derived from the dissolved salts on brewing processes and the character of beer.

Anticipating subsequent discussion of the influence on beer character of the mineral matter dissolved in brewing liquor, it may here be mentioned that gypsum and chalk have opposite effects in certain important respects, and that the effects of one may be counterbalanced by those of the other, if present in appropriate proportions. It is generally conceded that a moderate excess of the ions derived from gypsum or calcium sulphate is desirable for pale ales and that chalk or calcium carbonate is harmful, whereas a decreasing proportion of gypsum and increase of carbonates would be associated with sweeter, darker beers. Other salts occurring in relatively small quantities in the best natural brewing liquors have effects which will be noted in due course. Among these, sodium chloride or common salt, which may so easily gain access to wells in the neighbourhood of the sea coast or brine deposits, has a very definite influence on the character of beer. For these reasons the type of beer and the geology of the locality in which it is brewed are closely connected.

For some beers a very hard liquor is used. For others a very soft water is considered essential. Consideration of the liquors of Burton-on-Trent and Pilsen will show how widely the requirements differ. Though both towns are celebrated for their pale beers, the one for ale, the other for lager, the well waters at Burton-on-Trent contain an unusually high proportion of mineral sub-

stances, with gypsum as the main constituent, while the water used at Pilsen is extremely soft. For this reason hard gypseous liquor is generally considered essential for pale ales, while European lager brewers hold that a soft water is to be preferred for pale lager beers with pronounced bitterness. This may appear somewhat paradoxical, even when full allowance is made for the differences in materials and methods of brewing, together with the divergent characteristics of top and bottom fermentation beers. It suggests that undue weight has been attached to the total quantity of the different salts or ions present in the water and too little consideration given to a possible balance between the good and ill effects of the individual constituents and their relation to brewing materials and methods. It is certain that until recently water analyses have been regarded too literally, because there has been no guiding principle on which to base an interpretation. Even now their implications are to a large extent obscure and imitation of some well-known water is still, in most cases, considered to be the best guide to treatment of other waters, which may be thought to be deficient in some essential constituent or contain too much of another, disappointing as the results of such treatment are liable to be.

(311) Contamination of Water Supplies.

A constant check should be kept on the purity of brewing liquor from whatever source it may be derived, by periodical chemical and bacteriological examination. In this way only can chance pollution or infiltration of surface water be detected. There should be little chance of this in well-constructed deep borings, but the intensive pumping sometimes necessary in times of drought draws water from beyond the usual source of supply and may be accompanied by considerable change in the composition of the liquor, which would require revision of the usual methods of treatment for brewing. In some cases this may be associated with contamination but infiltration of surface water is more likely to occur during periods of excessive rainfall. Accidents of this kind can be detected by changes in the results of the usual analytical and bacteriological tests of a more marked kind than can be accounted for by seasonal variations. Such changes always give occasion for enquiry into the cause, followed if necessary by careful examination of the well or boring. Defects occasionally arise in bore tubes and cracks are liable to form in the lining walls of wells, through which extensive infiltration may occur, perhaps from cultivated fields or ditches. In such cases a more or less sudden rise in the free and albuminoid ammonia or chlorine content of the water occurs and bacteria typical of sewage may be found.

(312) Chemical Analysis.

It is not possible to determine with accuracy the quantity of organic matter in water, nor would such a determination have any practical value, since a large proportion may be of harmless vegetable origin and could not be differentiated chemically from organic matter derived from sewage or other dangerous sources. A number of chemical determinations are, however, commonly employed as criteria of organic purity but, as the quantity of organic matter is so small, the value of these methods of analysis must depend largely on the deductions which an experienced analyst can draw from them in regard to its origin. These determinations are detailed in Table 114, with the limits usually accepted for drinking waters and applicable to brewing liquors. It will be noticed that they depend on estimation of ammonia formed by decomposition of nitrogenous organic matter, of the nitrites and nitrates which result from its oxidation, of chlorine which occurs as common salt in urine to the extent of about 1%, and of the quantity of readily oxidisable matter, as measured by the oxygen absorbed from an acid solution of potassium permanganate.

TABLE 114.—ORGANIC PURITY OF WATER

Determination	Generally accepted limits
Free ammonia	0.01 part per 100,000.
Albuminoid ammonia	0.01 " "
Nitrites (NO_2')	0.2 part per 100,000.
Nitrates (NO_3')	3 parts per 100,000 if ammonia is high.
Chlorine	Contamination suggested by increase in a water normally containing little Cl.
Oxygen consumed	0.05 part per 100,000.

Decaying animal and vegetable matter yields ammonia, but rain falling upon manured ground may reach the subsoil water practically free from it, since nitrifying organisms convert it into nitrates. Nevertheless practically all waters contain some trace of ammonium salts, generally ammonium carbonate except in acid moorland waters in which it may be combined with other acids. The ammonia existing in this form is referred to as free or saline ammonia to distinguish it from the further quantity which can be obtained by distilling the water with a strong alkaline solution of potassium permanganate. This additional ammonia is produced by decomposition by the alkaline permanganate of any nitrogenous organic matter existing in the water and is known as "albuminoid ammonia." Free ammonia may be derived from sewage con-

tamination but it is not possible to draw definite conclusions from the quantity found, as this may be comparatively large in some waters quite free from sewage and some polluted waters contain very little ammonium salts. The quantity found in new bores or wells is frequently very high, but it will in many cases be found to be due to contamination during boring and will disappear when sufficient water has been pumped.

Useful information may, however, be obtained from the free ammonia in conjunction with the albuminoid ammonia. If the free ammonia is low and the albuminoid higher than that given in Table 114, they are generally assumed to be derived from vegetable matter, but if it is as high or higher than the albuminoid ammonia sewage pollution may be suspected, since free ammonia greatly exceeds the albuminoid in sewage and effluents. Free ammonia in excess of 0.01 part per 100,000, in presence of excess of organic matter, is thus strong presumptive, but not definite, evidence of sewage pollution, and many pure moorland waters could not pass this test.

There is a similar difficulty in interpreting the result of the test for nitrates. Although it is sometimes assumed that all the nitrates in water have resulted from the oxidation of nitrogenous organic matter by nitrifying bacteria, their presence can by no means be taken as a definite indication of dangerous pollution. The oxidation may have been so remote, that all accompanying bacteria would have been filtered off as the water percolated through the ground. In the presence of organic matter, with free and albuminoid ammonia approaching the limits, 3 parts per 100,000 of NO_3' may be an indication of pollution by animal matter but, in other cases, larger quantities of nitric acid are constantly found in waters about which there is no question of contamination. Nitrous acid is rarely found in waters, but may occur as an intermediate stage in the oxidation of organic matter to nitric acid or result from the reduction of nitric acid. Its occurrence in traces is, consequently, to be regarded with suspicion, as evidence of nearer approach to the original organic matter. It is equally difficult to assess the value of chlorine as an indication of pollution. In general it is derived from common salt in the strata, from beds of rock salt or sea-water infiltration, but occasionally an increase in the normal quantity found in any particular water may give rise to suspicion of infiltration from sewage or of urine.

It is clear from the above examples that the interpretation of the chemical analysis of waters in its applications to organic purity is hedged about with many*difficulties. Considerable experience and careful consideration of all available information

on the origin of the water is necessary before reliable conclusions on its purity can be drawn. The figures given in Table 114 as representing maximum quantities found with pure waters must thus be taken as no more than generally applicable. They are the limits usually permitted for drinking supplies and should not as a rule be exceeded in brewing waters. Excess almost always means contamination but very serious contamination is possible without any such chemical evidence. Definite proof of sewage pollution can only be obtained by detection of the pathogenic bacteria which make it dangerous.

(313) Microscopical Examination of Waters.

A microscopical examination of waters is always desirable in cases of turbidity or when suspended particles or sediment are present. In the majority of brewing waters, particularly when drawn from deep wells, the slight sediment which may form will be found to consist only of sand, iron oxide or other mineral matter, derived during the percolation of the water through sandy rocks. Shallow wells are, however, liable to inflow of surface water during rainy weather and this may bring with it various low forms of life, which are always liable to be found in streams, lakes, etc. In the course of time sand filters become choked with a slime of animal or vegetable origin. The flow becomes much reduced and the filtered water may be contaminated. A microscopical examination is particularly desirable whenever any unusual odour is noticed. Chemical examination may entirely fail to detect anything abnormal but the microscope may reveal protozoa or minute vegetable organisms and debris. Some of these can only exist in polluted waters, but there are others which live in pure water. It is difficult to distinguish these without special experience and, consequently, their occurrence in brewing waters should be treated with suspicion and the cause of contamination found. The liquor in exposed tanks is very liable to contamination by insects and, in some cases, by growth of vegetable matter or iron bacteria. Storage tanks should therefore be examined frequently and kept clean.

(314) Bacterial Contamination.

Bacterial contamination is not generally detected by microscopical examination of water sediments, for which cultures on solid nutrient media are required. Few waters are completely free from bacteria, but their number is not so important as their nature, for which special culture methods are used. Sewage may contain more than 1,000,000 per ml., including intestinal bacteria

and streptococci, so that infiltrations are greatly to be dreaded. Various standards of purity have been proposed but these cannot be taken as of much value, unless the necessary examination for pathogenic organisms is made, in which case a positive result showing the presence of very few cells per ml. would be much worse than the discovery of large numbers of non-pathogenic bacteria which would be killed when the water or wort is boiled. The following figures for bacterial counts are typical of the suggested standards.

Very pure water	..	0 to	10 bacteria per ml.
Very good water	..	10 to	100 „
Passable water	..	200 to	500 „
Impure water	..	500 to	1,000 „
Very impure water	..	over	1,000 „

A special sample in a small sterilised bottle must be taken for bacteriological examination, with every precaution to avoid contamination. The examination must be carried out as rapidly as possible after receipt of the sample and not more than 8 hours should elapse after collection of the sample, which should be placed in an ice chest if delay is unavoidable.

The methods usually adopted in the control of water supplies comprise determination of the total number of bacteria present in a given volume, and special tests for the presence of bacteria of the *coli-aerogenes* groups, such as *Es. coli* (*B. coli*) and *Aerobacter aerogenes*, which would indicate probable faecal contamination, although some similar strains are merely soil types. Deep bore waters generally contain less than 10 cells per ml., though some waters from the chalk contain many more. The colony counts are, however, of little use unless they are carried out at regular intervals, when any increase would demand explanation, if it could not be attributed to normal seasonal variations. 100 to 200 colonies per ml. are not infrequently obtained from potable waters, but most of the organisms would be non-pathogenic and harmless in brewing, since they would be destroyed by boiling in the slightly acid hopped wort, if not in the preliminary boiling of the mash liquor. Larger counts would be regarded with suspicion and might possibly give rise to beer infection, if the water was used for bottle rinsing.

The *Coli-aerogenes* or “ presumptive coli ” test in a lactose-bile salt medium, frequently referred to as the MacConkey test, is the most generally used bacteriological index of pollution. It is carried out by incubating measured quantities of the water in solid or liquid media containing bile salt, sodium taurocholate, which prevents the growth of other bacteria, lactose and an indi-

cator. The presence of bacteria of the *coli-aerogenes* groups is indicated by the formation of gas and acid in the liquid medium and of red colonies on the solid. The test is based on the assumption that the smallest volume of water giving these *coli* reactions contains one viable bacillus of the group. It is prudent to assume that faecal or sewage contamination exists if a positive result is obtained with 10 ml. of the water, that is if 10 or more cells exist in 100 ml., but a positive test with 5 ml. may be accepted as a safe limit for brewing waters. *Es. coli* is, however, frequently found in moorland waters, in which no sewage or dangerous contamination can be suggested, but a negative MacConkey test is usually a reliable indication of purity.

The bacterial counts are usually made on nutrient agar in Petri dishes. Gelatin is liable to liquefy and therefore is not so convenient. The cultures are made at 22° and 37° C. (71·6° and 98·6° Fahr.) Most bacteria developing at 22° but not at 37° are harmless to health, but a high count should not be considered as immaterial, since it gives an indication of the amount of material available for bacterial nutrition or of the quantity of dust, etc., which may have gained access to the water. The count at 37° C. affords information on the dangerous pollution, since most of the harmless water bacteria will not grow at this temperature. Those that do grow are mainly of sewage or intestinal origin. An increase in the number of bacteria which will grow at 22°, without any rise in the count at 37°, frequently occurs after heavy rain.

(315) Iron Bacteria and Iron in Water.

Great annoyance is occasionally caused through the formation of slimy masses in tanks or blockage of pipes by development of thread-like "iron bacteria." Among the commonest species are *Leptothrix ochracea* and *Crenothrix polyspora*, which form threads 2 to 3 mm. or more in length and become coated with a brown slime containing iron. They thrive in waters containing iron and organic matter, but may obtain the iron they require from pipes and tanks. In presence of manganese the slime is black. As they are inhibited by alkalinity, their eradication can be effected by addition of lime, followed by sedimentation and filtration.

Iron is itself objectionable in brewing, since it may affect the colour, flavour and brilliance of the beer. When dissolved in wort it forms black tannate of iron with hop tannin and may darken the yeast or detrimentally influence the foam on the beer and cause it to collect in patches. A large proportion of waters contain a trace of iron, but up to about 1 part per 100,000 should in most cases not lead to trouble. It generally occurs as ferrous bicarbonate, but may exist in organic combination in peaty waters.

A large proportion of the iron present is precipitated with the carbonates when the water is boiled or treated with lime. On exposure of the water to air, the iron is oxidised to colloidal ferric oxide and precipitated, sometimes giving an opalescence to water which was quite clear when collected and occasionally forming large deposits in tanks. Methods of purification based on oxidation are made use of under circumstances in which the character of the beer might be affected by traces of iron, particularly for pale lager beers.

Traces of manganese are frequently associated with iron. The quantity present is not generally separately determined in water analyses but is included with the iron. Traces of other heavy metals are also found in some natural waters, but should not be present in brewing liquors. Lead, zinc and copper may, in addition, be dissolved from mains, particularly by very soft waters. The deposit of carbonate from hard waters prevents this attack on the mains and it is very unusual to find more than the most insignificant trace of any of them.

(316) Heavy Water and Rare Elements.

The known physiological effects of minute quantities of certain elements and their influence on plant growth have given rise to speculation on their possible effects in brewing liquors, but no facts have yet been found to show that they have any influence at all in brewing. Among the elements which occur in minute traces in water are some with radio-active properties and here again the problem of possible influence on fermentation arises. The principal radio-active elements are radium, thorium, actinium and polonium and a trace of some of these may gain access to water during its passage through the rocks. By disintegration these give rise to other elements, such as the emanation of radium, to which the radio-activity of water is probably mainly due. When radio-active water is boiled, the emanation passes off with the dissolved gases and the water loses its radio-active properties. For this reason, apart from the minuteness of the measurable radio-activity, it is hardly to be anticipated that radio-activity plays any part in fermentation phenomena, but it is to be remembered that if radium is present the active emanation will again be formed in time.

The presence of heavy water in greater or smaller quantity might with greater probability be anticipated to influence the behaviour of brewing liquor, but here again nothing is yet known. Heavy water is the compound, D_2O , of heavy hydrogen, Deuterium or Diplogen, corresponding to water, formed by its combination with oxygen. The heavier form of hydrogen always exists

with hydrogen and heavy water appears to occur in all natural waters, generally to the extent of about one part in 9,000. It is a liquid with the same appearance as water, but is 10% heavier, freezes at 38.8° Fahr. and boils at 214.5° . It can be separated from water by very tedious processes of fractional distillation or electrolysis. The residues in old electrolytic cells contain up to about 1 part in 2,700 and its concentration in ordinary water increases as the latter is evaporated. High concentrations have been claimed to have a detrimental effect on fermentation and to be toxic to micro-organisms and small animals, so that it is at least possible that varying quantities in brewing liquors may have some influence on the course of fermentation, or explain the different behaviour of liquors which are apparently similar in composition. No evidence has yet, however, been obtained to support or contradict these speculations.

Another question which does not appear to have been definitely settled is whether chlorinated water has any deleterious influence on fermentation. Brewers have certainly recorded defective fermentations during periods of draught, which they have attributed to the effect of chlorinated city supplies and, possibly, with reason when these have been improperly treated.

MINERAL CONSTITUENTS OF BREWING LIQUORS

(317) Analysis of Water.

Until recently it has been customary to express the results of water analysis in terms of basic and acidic oxides, such as Na_2O , CaO , SO_3 , etc., but expression of the results in terms of the ions into which the salts are believed to be almost completely dissociated in dilute solutions is now gaining favour, since it should more accurately represent the constituents of the water. The quantity of each base, acid radical or ion is variously given in parts per million (mgm. per litre), parts per 100,000 or grains per gallon. The last is very commonly used in England and America but, since the United States gallon of water weighs 8.3389 lb. at 39.2° Fahr. and 30 inches barometric pressure or 8.333 lb. at 60° Fahr. as compared with the Imperial gallon of 10 lb. at 62° Fahr. and 30 inches pressure, confusion may arise if analyses are expressed in grains per gallon without specification of the particular gallon referred to. In England grains per gallon is equivalent to parts per 70,000, in America to parts per 58,800.

This diversity has led to the proposal that parts per million should be adopted as an international standard.¹ Whichever

basis of expression is used the analytical results can be readily converted from one to another. Milligrams per litre divided by 10 gives parts per 100,000 and the latter multiplied by 0.7 gives grains per Imperial gallon.

(318) The Millival.

The most convenient way to express the strength of solutions when their chemical reactions are in question is in terms of "normality," a "normal solution" being defined as that which contains the "equivalent weight" in grams of the solute per litre. Decinormal, centinormal and millinormal solutions contain respectively a tenth, a hundredth or a thousandth of these quantities per litre. The equivalent weight of an element is that weight which will combine with unit weight of hydrogen or with the weight of some other element which in its turn would combine with unit weight of hydrogen. In many cases this is the same as the atomic weight of the element. Thus 35.5, the atomic weight of chlorine, is also its equivalent weight, because it combines with 1 part by weight of hydrogen to give 36.5 parts by weight of HCl. Similarly 23 is the atomic and equivalent weight of sodium, because it combines with 35.5 parts by weight of chlorine to give 58.5 parts by weight of NaCl. Other elements combine with two, three, four, five or six atoms of hydrogen and their equivalent weight is found by dividing their atomic weight by 2, 3, 4, 5 or 6. Thus 32 parts by weight of sulphur or 16 parts by weight of oxygen combine with 2 parts by weight of hydrogen in H_2S or H_2O and their equivalent weights are half their atomic weights or 16 and 8 respectively.

The weights of compounds containing one atom of reactive hydrogen or an equivalent weight of some other element or group are regarded as equivalent. Thus 36.5 parts by weight of HCl ($1 + 35.5$) is equivalent to 40 parts by weight of NaOH ($23 + 16 + 1$) and both of these are equivalent to 49 parts of H_2SO_4 , $\left(\frac{2 + 32 + 64}{2}\right)$ or 37 parts of Ca(OH)_2 , $\left(\frac{40 + 32 + 2}{2}\right)$. Normal solutions of these substances would contain the weights given for each in grams per litre, their gram-equivalents per litre.

Since brewing liquors are solutions of salts, the amount of each salt dissolved may be expressed in terms of normality equally well as in grains per gallon or mgms. per litre, with the advantage that the properties of the water are thereby more clearly shown. The quantities dissolved are generally so small that they are most conveniently given in terms of millinormality, that is in milligram-equivalents per litre. The term "Millival" is used for this unit. The number of millivals of any element or ion present is found

by dividing the analytical figure in parts per million by the equivalent weight of the element or ion. The figures thus obtained are generally convenient for calculation, while the corresponding value obtained from analytical results in grains per gallon or parts per 100,000 is frequently inconveniently small. Apart from this the method of calculation described can be applied equally well to analyses expressed in parts per million, parts per 100,000 or grains per gallon.

This method of expression will be found so greatly to facilitate the interpretation of water analyses or calculation of hypothetical combinations in the form of salts that it will be used in all the type analyses given. The analyses are also all given in ionic form and not in terms of basic and acidic oxides. The more important ionic constituents of brewing liquors are given below with their approximate equivalent weights. In the case of monovalent ions, the equivalent weight is the atomic weight of the element or the sum of the atomic weights of the group of elements constituting the ion. In the case of divalent or trivalent ions it is one-half or one-third of the atomic weight or sum of the atomic weights. The signs ' and ' are used instead of - or + to denote the sign of the electric charge borne by each ion, the signs '' and '' expressing the double negative or positive charges carried by divalent ions. The ions are called anions or cations according as they are negatively or positively charged and travel to the anode (positive pole) or cathode (negative pole) when an electric current is passed through the solution in which they occur. Anions and cations bearing equal but opposite electric charges combine to form salts in which the charges may be considered as neutralised. A divalent metallic ion or cation marked with '' requires two monovalent acid ions or anions for complete discharge or salt formation and similarly a divalent anion combines with two monovalent cations. The most important ions produced by the salts dissolved in brewing liquor and their equivalent weights are :

Anions	..	NO ₃ '	Cl'	SO ₄ ''	HCO ₃ '	CO ₃ ''
		62	35.5	48	61	80
Cations	..	K'	Na'	Mg''	Ca''	
		39	23	12	20	

An example may be given to show the use of the equivalent weights given below each ion. Thus a water containing 21 grains per gallon of calcium, which is the same as 300 parts per million or 300 milligrams per litre, contains $\frac{300}{20} = 15$ millival of calcium.

These would be exactly equivalent to or able to combine with 15 millival of SO₄'' or Cl' or CO₃'', that is with $15 \times 48 = 720$ milli-

grams per litre or 50·4 grains per gallon of SO_4 ; $15 \times 35\cdot5 = 532\cdot5$ milligrams per litre or 37·275 grains per gallon of Cl; or $15 \times 30 = 450$ milligrams per litre or 31·5 grains per gallon of CO_3 .

Iron, aluminium and silicic acid or silica are also usually found in natural waters in quantities of about 2 or 3 parts per 100,000. It will not be necessary to consider these in the type analyses, although the removal of iron by oxidation or other means is sometimes necessary and the silicic acid may have a definite influence in some cases on the brewing quality of water. The small quantity of potassium generally present is also not given in the Tables but its equivalent as sodium is included in the figures for that element. Carbonic acid should be expressed as HCO_3 to represent the anion of the soluble calcium and magnesium bicarbonates, though a small quantity may exist as CO_3 . It is, however, more conveniently given as CO_3 in order that a direct comparison may be made between the total weight of ions found and the weight of the total solids dried at 180°C . This convention is accordingly adhered to in the analyses given.

(319) Expression of Analytical Results.

The analysis of a very hard water from a bore at Burton-on-Trent is taken as an example of the ionic method of expressing analytical results and calculation of the hypothetical saline constituents of water. The analysis was given by Lott² in the form shown in Table 115.

TABLE 115.—ANALYSIS OF BURTON-ON-TRENT BORE WATER

	Parts per 100,000
Carbonate of lime	20·0
Carbonate of magnesia	3·0
Sulphate of lime	170·0
Sulphate of magnesia	35·0
Sulphate of soda	2·0
Nitrate of magnesia	4·0
Chloride of magnesia	1·0
Chloride of sodium and potassium	10·0
Difference = silica, iron, alumina, etc.	2·0
Total solids dried at 180°C	247·0

The individual bases and acidic oxides, calculated from these

figures, are set out in the old way in the first column of Table 116, with the corresponding ions in parts per million in the second. These divided by their equivalent weights are given as millival in the last column, headed N/1000, meaning millinormality or milligram-equivalents per litre. The figures are rounded off to the first decimal place. It will be noted that the sum of the millivalents representing cations equals that of the anions. This in itself provides a useful check on analyses but it is practically impossible that analyses should be so accurate as exactly to check in this way and it is generally desirable to round off the alkali metals, which are very often found by difference rather than by actual determination.

TABLE 116.—ANALYSIS OF BURTON-ON-TRENT BORE WATER
(GIVING IONS AND MILLIVALS)

Original analysis parts per 100,000		Ions, parts per million		Millivalents of ions N/1,000	
K ₂ O & Na ₂ O	6.17	K ⁺ & Na ⁺	45.8	K ⁺ & Na ⁺	2.0
MgO	14.48	Mg ⁺⁺	87.5	Mg ⁺⁺	7.3
CaO	81.20	Ca ⁺⁺	580.0	Ca ⁺⁺	29.0
N ₂ O ₅	2.92	NO ₃ [']	33.5	NO ₃ [']	0.6
Cl	6.82	Cl [']	68.2	Cl [']	1.9
SO ₃	124.46	SO ₄ ^{''}	1493.5	SO ₄ ^{''}	31.1
CO ₂	10.37	CO ₃ ^{''}	141.0	CO ₃ ^{''}	4.7
Total solids dried at 180° C., 247.0 parts per 100,000					

TABLE 117.—HYPOTHETICAL SALINES

Salts	Millivalents × equivalents	Salts, parts per		Salts, grains per gallon
		1,000,000	100,000	
Sodium nitrate	0.6 × 85	51.0	5.10	3.57
Sodium chloride	1.4 58.5	81.9	8.19	5.73
Magnesium chloride ..	0.5 47.5	23.7	2.37	1.66
Magnesium sulphate ..	6.8 60	408.0	40.80	28.56
Calcium sulphate	24.3 68	1652.4	165.24	115.67
Calcium carbonate	4.7 50	235.0	23.50	16.45
Total solids	—	2452.0	245.20	171.64

(320) Saline Constituents of Water.

According to the generally accepted theory that strong electrolytes are completely dissociated into their component ions in dilute aqueous solutions, no salts of strong acids and bases can exist in brewing liquors, which are essentially dilute solutions of metallic salts. Gypsum, common salt, calcium bicarbonate, etc., are thus believed to be non-existent in waters in which the quantities of their ions, Ca^{++} , Na^+ , SO_4^{--} , Cl^- and HCO_3^- have been determined by analysis. Any attempt to express the analytical results in such a form as would suggest that the salts actually exist in the water in the proportions stated would be in contradiction to the theory of electrolytic dissociation and, so far as is known, would have no basis in reality. It is, however, convenient to calculate the "hypothetical saline constitution" of the water in order to obtain an idea of the quantities of salts which must be dissolved in distilled water to yield a solution which would give similar figures on analysis. In many cases it is helpful in the treatment of brewing liquors, giving a more concrete idea of their composition to those unfamiliar with the conception of ions. It must, nevertheless, be emphasised that figures given in this form are entirely arbitrary and represent only one out of a very large number of mixtures of salts which would give liquors of the same composition when dissolved in the same quantity of distilled water.

For example, if equivalent quantities of calcium sulphate, magnesium sulphate and sodium carbonate are dissolved in cold distilled water, the total concentration being similar to that in a natural water, say 30 grains per gallon, an analyst would find equivalent quantities of Ca , Mg , Na , and CO_3 with two equivalents of SO_4 . He might combine these ions as calcium sulphate, sodium sulphate and magnesium carbonate or as magnesium sulphate, sodium sulphate and calcium carbonate, or as calcium sulphate, magnesium sulphate and sodium carbonate, all of which would agree equally well with his analysis. It is therefore advisable to take the individual cations and anions in a definite order, rather than attempt to decide on the merits of each particular case, whenever it is thought desirable to indicate possible combinations. In this way only can uniformity be secured in reports from different analysts.

Although the order in which the ions are combined must be arbitrary, it should suggest the probable behaviour of the water under significant conditions. Thus with brewing liquors it is desirable that the list of salts given in the analyst's report should suggest what is likely to happen when the water is raised to mashing heat or boiled. This has a particular bearing on the order in which

calcium and magnesium are combined with the acid ions. If magnesium is taken first as sulphate, it leaves more of the calcium with the carbonate ions, which suggests precipitation of calcium carbonate on boiling or when the water is softened with lime. This order of combining the ions is contrary to that adopted in the International Register of Spas and Medicinal Waters and is probably not so well justified in the cold water as calcium—magnesium. It also leads to the suggestion that the water contains magnesium sulphate, when calcium sulphate would look better. It is, however, adopted here for brewing waters to suggest that calcium carbonate is first removed and the order used is :

Cations : Potassium, Sodium, Magnesium, Calcium.

Anions : Nitrate, Chloride, Sulphate, Bicarbonate, Carbonate.

According to this rule, the hypothetical salines given by the analyst of the above-mentioned dilute solution of calcium sulphate, magnesium sulphate and sodium carbonate would be sodium sulphate, magnesium sulphate and calcium carbonate. This does not give the actual salts used in making up the solution but it does suggest what happens when the mixed solution is boiled. No precipitation occurs when a dilute solution of sodium carbonate is added to a dilute solution of calcium sulphate and magnesium sulphate, the salts being in equivalent proportions. When, however, the temperature is raised to 170° Fahr., a copious precipitate consisting of calcium carbonate only is precipitated, while Ca^{++} and CO_3^{--} can still be found in the filtered water in equivalent quantities corresponding with 2.2 grains per gallon of CaCO_3 which represents the solubility of calcium carbonate in pure water. The combination of magnesium with sulphate and calcium with carbonate suggests this course of events, but is in no way intended to imply that the ions are combined in that way in the solution.

The procedure adopted in combining the ions in the order given is as follows, taking the analysis of Burton water in Table 116 as an example and using the millival's given in the last column of the Table to simplify the calculations.

0.6 millival of NO_3 is combined with 0.6 of Na giving 0.6 millival NaNO_3 and leaving $2.0 - 0.6 = 1.4$ millival of Na.

1.4 millival of Na is combined with 1.4 of Cl giving 1.4 millival of NaCl and leaving $1.9 - 1.4 = 0.5$ millival of Cl.

0.5 millival of Cl is combined with 0.5 of Mg giving 0.5 millival MgCl_2 and leaving $7.3 - 0.5 = 6.8$ millival's of Mg.

6.8 millival's of Mg is combined with 6.8 of SO_4 giving 6.8 millival's MgSO_4 and leaving $31.1 - 6.8 = 24.3$ millival's of SO_4 .

24.3 millival's of SO_4 is combined with 24.3 of Ca giving 24.3 millival's CaSO_4 and leaving $29.0 - 24.3 = 4.7$ millival's of Ca.

4.7 millivals of Ca is finally combined with the 4.7 millivals of CO_2 giving 4.7 millivals of CaCO_3 .

The millivals of the combinations so found are then multiplied by their respective equivalent weights as in Table 117 to give the hypothetical salines in parts per million, from which the corresponding quantities as parts per 100,000 or grains per gallon are calculated as desired.

It will be noted that the salts found in this way differ from those given by Lott in the original analysis, but the two statements correspond equally well with the analytical results. The balance of cations and anions must be exact in any solution, but it cannot be expected that such accuracy would be shown by a water analysis and it is usually necessary to round off the results, as has been done in the example given.

(321) Hardness of Water.

The term "hardness" is used to express the quantity of calcium and magnesium salts in water with reference to their property of destroying soap by forming insoluble calcium and magnesium salts of the fatty acids and so preventing the production of foam. *Degrees of hardness* are calculated from the amount of a standard soap solution which must be added to a measured volume of the water to produce a lasting foam on shaking. They are expressed in various ways in different countries, the amount of soap destroyed being converted to its equivalent either of calcium carbonate or calcium oxide, whether the actual reaction was with carbonate, sulphate, chloride or nitrate of calcium or magnesium.

English or Clark degrees represent grains per Imperial gallon of CaCO_3 .

German degrees are parts per 100,000 of CaO .

French degrees are parts per 100,000 of CaCO_3 .

In America hardness is expressed in parts per million, or grains per American gallon of CaCO_3 .

French degrees can be converted to Clark degrees by multiplying by 0.7 (70,000 grains per gallon). The corresponding factor for German degrees is 1.25 and that from grains per American gallon (58,800) to English is 1.2.

Temporary hardness is that due to calcium and magnesium dissolved in the water as bicarbonates and precipitated as carbonates on boiling, as the excess of CO_2 is driven off. Water is also softened in the same manner by standing for a long time exposed to the air. The term temporary hardness is rather misleading, since neither calcium nor magnesium carbonate are completely precipitated by boiling. About 2.2 grains per gallon of the former and 10 grains per gallon of magnesium carbonate

remain in solution after boiling. A more accurate estimate of the carbonates present is obtained by titration of a known volume of the water by N/10 acid. Usually this measures the quantity of calcium and magnesium carbonates, that is the carbonate hardness, but occasionally sodium carbonate is also present.

Permanent hardness expresses the quantity of chlorides, sulphates and nitrates of calcium and magnesium, together with the proportion of carbonates not removed by boiling. The temporary and permanent hardness together give the total hardness. Waters may be classified in an arbitrary manner as soft, moderately soft, moderately hard, hard and very hard but there is no fixed scale to demarcate the groups. Waters containing up to 7 Clark degrees of hardness may be considered as soft, from that to 15° as moderately soft, 15 to 25° as moderately hard, 25 to 35° as hard and above 35° very hard.

(322) p_H of Waters.

Although the hydrogen ion concentration of wort is of great importance in brewing, that of the water itself is of less significance, but a colorimetric determination of its p_H may give certain information. Thus, if the p_H is greater than 8, the water may be considered to contain no free CO_2 , but carbonates or bicarbonates are present. Most waters have a p_H between 6 and 8, usually around the point of neutrality, p_H 7. If the p_H value is lower than 7 and rises to 7 or above after boiling, carbonic acid is the only free acid present. Soft surface waters derived from moorlands generally contain humic acid, with sulphur compounds, and may have a p_H of 5 or 4.5 which does not rise to 7 on boiling. Such waters have a very corrosive action on iron, lead and, to a smaller extent, on copper. Most soft waters attack these metals to some extent.

BREWING LIQUORS

(823) Typical Brewing Liquors.

The influence of brewing liquors of varying saline composition on the character of beers brewed from them should be studied, in the first instance, by comparing the analyses of waters from a few well-known brewing centres and the characteristics of the beers typical of those places. This should be followed up by making experimental brews with waters of known composition and examination of the worts and beers obtained. The analyses of natural brewing liquors given in the following tables show the salient characteristics of liquors suitable for different types of beer, but they have been simplified in certain respects. Potassium is not repre-

sented although a small quantity is found in some of the waters. Its equivalent as sodium has been added to the quantity of the latter found. CO_3 is also used in place of HCO_3 , while silica, iron and aluminium have been omitted, although they amounted in most cases to 1 or 2 parts per 100,000.

The ratio $(\text{Ca}'' + \text{Mg}'') : \text{CO}_3''$, given as a distinctive character for each water and used in later tables as a basis of classification, means the ratio between the quantities of calcium plus magnesium and the carbonate ions. This is not based on the actual weights of calcium, magnesium and carbonate ions in parts per 100,000 or grains per gallon as found by analysis, but by the quantities of these ions in terms of normality, which give the chemical equivalence of the quantities present. These are found by dividing the analysis figures by the equivalent weights of the ions and represent millival, when expressed in parts per 1,000,000. The sum of the millival of calcium and magnesium so found is expressed as 100 and the millival of the carbonate ions are given as a proportion of this. The result is the carbonate ratio $(\text{Ca}'' + \text{Mg}'') : \text{CO}_3''$. The term "ionic balance" is used in Table 118 to express the relation between all the ions present, calculated from the analysis in terms of millinormality or millival, the value of 100 being allotted to the sum of the millival of all the ions.

(324) Burton-on-Trent Waters.

The analysis given in Table 115 represents one of several types of water of markedly different composition obtained from wells of different depths at Burton-on-Trent. The variations in mineral constitution are greater than is usual in an equally restricted area but it must be noted that differences of similar nature occur elsewhere and that the analyses given in the following pages as representing waters of well-known brewing centres should be taken only as types, from which considerable variations may occur. Lott^a divided the wells and bores of Burton-on-Trent in four groups, according to the strata reached, viz., Gravel beds, Upper Keuper marls, Lower Keuper sandstones and the Bunter conglomerates. Although the last formation falls stratigraphically below the others, it is faulted up in the north-east of the town so that the depths of the bores reaching into it are not so great as those into the Lower Keuper sandstones adjacent to it. He further divided the waters from the shallow wells in the gravel beds in two groups, according as their total solids were greater or less than 100 parts per 100,000 and those of the bores in the Upper Keuper marls in two groups with total solids above and below 200 parts per 100,000. There is considerable variation in the waters from different wells in the same category, but the general characteristics of the six groups are repre-

sented in Table 118, compiled from Lott's average analyses of a large number of samples of each group. These show differences in total solids ranging from 68 to 247 parts per 100,000, which are attributable to the nature of the rock formations reached at different depths, to the irregular distribution of gypsum in the area from which the waters were drawn and the existence of extensive faults. The differences in composition are very clearly shown by the ionic balance. An analysis of medium hardness has been taken as typical of Burton-on-Trent pale ale waters. The very hard water of which the analysis is given in Table 115 is too hard for the lighter beers of to-day, tending to yeast weakness and stench, while the water from the Bunter Conglomerate would not be used for brewing, with waters of the other types available.

TABLE 118.—TYPES OF WATER FROM WELLS AT BURTON-ON-TRENT
(PARTS PER 100,000)

No. of samples averaged	Shallow wells			Artesian bores				
	20-32 ft. gravel beds			70-200 ft. U. Keuper marl			350-550 ft. L. Keuper sandstone	180-400 ft. Bunter Conglom- erate
	20	20	200	10	5	50	3	2
Total solids	below 100	above 100		above 200	under 200			
Sodium nitrate ..	6.8	13.6	10.2	5.1	7.6	6.0	—	—
„ chloride ..	6.4	3.5	4.7	8.2	7.0	7.6	40.9	18.7
„ sulphate ..	—	—	—	—	—	—	24.0	10.5
Magnesium chloride ..	5.7	10.0	8.1	2.4	3.3	2.9	—	—
„ sulphate ..	17.4	30.6	24.0	40.8	34.8	37.2	24.0	12.0
„ carbonate ..	—	—	—	—	—	—	—	0.8
Calcium sulphate ..	21.8	52.4	37.4	165.2	89.1	142.1	80.2	—
„ carbonate ..	23.0	29.0	25.5	23.5	22.5	23.5	22.0	26.0
Silica, iron, aluminium	0.9	0.9	1.1	1.8	0.7	0.7	2.9	—
Total solids	82.0	140.0	111.0	247.0	165.0	220.0	194.0	68.0

IONIC BALANCE, TOTAL MILLIEQUIVALENTS OF IONS AS 100

Total solids	Na	Mg	Ca	NO ₃	Cl	SO ₄	CO ₃	Carbonate ratio
82.0 ..	6.9	14.8	28.3	2.9	8.3	22.1	16.7	39
140.0 ..	4.8	15.7	29.5	3.5	5.9	27.9	12.7	28
111.0 ..	5.5	15.6	28.9	3.3	6.8	26.0	13.9	31
247.0 ..	2.6	9.5	37.9	0.8	2.5	40.6	6.1	13
165.0 ..	3.4	12.6	34.0	1.1	3.6	36.6	8.7	19
220.0 ..	2.9	9.9	37.2	1.0	2.8	39.4	6.8	15
194.0 ..	17.0	6.5	26.5	—	11.4	31.4	7.2	22
68.0 ..	19.4	9.2	21.4	—	13.2	14.5	22.3	73

(325) Type A. Burton-on-Trent Water.

The analysis given in Table 119 may be taken as typical of waters suitable for brewing pale ales. It is characterised by high total solids in which calcium and sulphate ions predominate, with a much lower proportion of magnesium and carbonate and insignificant quantities of sodium, chlorine and nitrate ions. The ions hypothetically combined as salts show a predominance of calcium sulphate, with about one-half the quantity of magnesium sulphate and one-third of calcium carbonate, sodium chloride and nitrate representing a very small portion of the total solids of 122 parts per 100,000. Waters of this character appear to be unsurpassed for pale ales and are used without treatment of any sort, other than boiling for half an hour or an hour previous to reducing to mashing temperature. They are also satisfactory for strong ales and produce excellent mild ales of full gravity.

TABLE 119.—BURTON-ON-TRENT WATER

$$(\text{Ca}^{++} + \text{Mg}^{++}) : \text{CO}_3'' = 100 : 25$$

	Ions		Salts			
	Millivals	Parts per 100,000		N/1000	Parts per 100,000	Grains per gallon
Sodium, Na ⁺ ..	1.3	3.0	NaNO ₃	0.5	4.2	2.9
Magnesium, Mg ⁺ ..	5.2	6.2	NaCl	0.8	4.7	3.3
Calcium, Ca ⁺ ..	13.4	26.8	MgCl ₂	0.2	1.0	0.7
Nitrate, NO ₃ ' ..	0.5	3.1	MgSO ₄	5.0	30.0	21.0
Chloride, Cl'' ..	1.0	3.6	CaSO ₄	8.7	59.2	41.4
Sulphate, SO ₄ '' ..	13.7	63.8	CaCO ₃	4.7	23.5	16.5
Carbonate, CO ₃ ''	4.7	14.1	—	—	—	—
	—	122.6	—	—	122.6	85.8

(326) Type B. Dortmund Water.

This water resembles that of Burton-on-Trent in the predominance of CaSO₄ but differs from it in that the total solids are less and the carbonate ratio greater. Sodium and chlorine are present in greater quantity and are represented as sodium chloride. Waters of this type are well known for medium hopped lager beers which attenuate well. The Dortmund lagers are not so pale and dry as those of Pilsen, nor nearly so sweet and full as the dark Munich beers. Similar waters are very successfully used for brewing pale ales.

TABLE 120.—DORTMUND WATER
(Ca⁺⁺ + Mg⁺⁺) : CO₃^{''} = 100 : 60

	Ions		Salts			
	Millivials	Parts per 100,000		N /1000	Parts per 100,000	Grains per gallon
Sodium, Na ⁺ ..	3.0	6.9	NaCl	3.0	17.5	12.2
Magnesium, Mg ⁺⁺	1.9	2.3	MgSO ₄	1.9	11.4	8.0
Calcium, Ca ⁺⁺ ..	13.0	26.0	CaSO ₄	4.0	27.2	19.5
Chloride, Cl ⁻ ..	3.0	10.6	CaCO ₃	9.0	45.0	31.5
Sulphate, SO ₄ ^{''}	5.9	28.3	—	—	—	—
Carbonate, CO ₃ ^{''}	9.0	27.0	—	—	—	—
	—	101.1	—	—	101.1	71.2

(327) Type C. Edinburgh Water.

The analysis of Edinburgh water given in Table 121 represents a supply from the Old Red Sandstone. In total solids and carbonate ratio it approaches waters of the Dortmund type, but differs from the waters previously given in containing a greater quantity of sodium. SO₄^{''} is the predominant anion but gypsum is not represented among the salts, as the Ca⁺⁺ and CO₃^{''} are equivalent. Following the convention explained in the previous chapter, SO₄^{''} is given as if combined as sodium and magnesium sulphates but it must be recalled that the existence of the salts in the water is entirely hypothetical. Edinburgh is well known for its pale ales.

TABLE 121.—EDINBURGH WATER
(Ca⁺⁺ + Mg⁺⁺) : CO₃^{''} = 100 : 70

	Ions		Salts			
	Millivials	Parts per 100,000		N /1000	Parts per 100,000	Grains per gallon
Sodium, Na ⁺ ..	4.0	9.2	NaNO ₃	0.5	4.2	2.9
Magnesium, Mg ⁺⁺	3.0	3.6	NaCl	1.7	10.0	7.0
Calcium, Ca ⁺⁺ ..	7.0	14.0	Na ₂ SO ₄	1.8	12.8	9.0
Nitrate, NO ₃ ⁻ ..	0.5	3.1	MgSO ₄	3.0	18.0	12.6
Chloride, Cl ⁻ ..	1.7	6.0	CaCO ₃	7.0	35.0	24.5
Sulphate, SO ₄ ^{''} ..	4.8	23.1	—	—	—	—
Carbonate, CO ₃ ^{''}	7.0	21.0	—	—	—	—
	—	80.0	—	—	80.0	56.0

(328) Type D. London M.W.B. Water.

The analysis in Table 122 is typical of the domestic supplies of many cities and of other waters drawn from chalk formations. The total solids are usually between 25 and 40 parts per 100,000 and the carbonate ratios between 100 : 80 and 100 : 90. Calcium carbonate is the predominant salt, with significant quantities of sodium and magnesium chlorides and sulphates. They form excellent brewing waters for mild ales and stouts and are useful for pale ales, after removal of carbonates and treatment with gypsum. Many waters from the chalk contain significant quantities of nitrates which may render them less suitable for brewing.

TABLE 122.—LONDON M.W.B. WATER

(Ca⁺⁺ + Mg⁺⁺) : CO₃^{''} = 100 : 86

	Ions		Salts			
	Millivals	Parts per 100,000		N/1000	Parts per 100,000	Grains per gallon
Sodium, Na ⁺ ..	1.05	2.4	NaNO ₃	0.05	0.4	0.3
Magnesium, Mg ⁺⁺ ..	0.3	0.4	NaCl	0.5	2.9	2.0
Calcium, Ca ⁺⁺ ..	4.5	9.0	Na ₂ SO ₄	0.5	3.6	2.5
Nitrate, NO ₃ ['] ..	0.05	0.3	MgSO ₄	0.3	1.8	1.3
Chloride, Cl ['] ..	0.5	1.8	CaSO ₄	0.4	2.7	1.9
Sulphate, SO ₄ ^{''} ..	1.2	5.8	CaCO ₃	4.1	20.5	14.4
Carbonate, CO ₃ ^{''} ..	4.1	12.3	—	—	—	—
	—	32.0	—	—	31.9	22.4

(329) Type E. Dublin and Munich Waters.

The brewing waters of Dublin and Munich are very similar in composition and are regarded as ideal for the types of stout and dark lager beer for which these cities are respectively renowned. With total solids of between 20 and 30 parts per 100,000, they are characterised by an almost exact equivalence between the calcium plus magnesium and carbonate ions, which would be represented by 100 : 100. They can be treated for pale beers by removal of carbonates and gypsum additions.

TABLE 123.—MUNICH WATER
 $(\text{Ca}^{++} + \text{Mg}^{++}) : \text{CO}_3'' = 100 : 97$

	Ions		Salts			
	Millivalls	Parts per 100,000		N/1000	Parts per 100,000	Grains per gallon
Sodium, $\text{Na}^+ \dots$	0.05	0.1	NaNO_3	0.05	0.4	0.3
Magnesium, Mg^{++}	1.60	1.9	MgCl_2	0.05	0.2	0.1
Calcium, $\text{Ca}^{++} \dots$	4.00	8.0	MgSO_4	0.1	0.6	0.4
Nitrate, $\text{NO}_3' \dots$	0.05	0.3	MgCO_3	1.45	6.1	4.3
Chloride, $\text{Cl}' \dots$	0.05	0.1	CaCO_3	4.0	20.0	14.0
Sulphate, $\text{SO}_4'' \dots$	0.10	0.5	—	—	—	—
Carbonate, CO_3''	5.45	16.4	—	—	—	—
	—	27.3	—	—	27.3	19.1

(330) Type F. London Deep Well Water.

Waters from deep bores through the London Clay into the underlying strata were formerly used for brewing full, sweet stouts but they are not now used and cannot be looked upon as good brewing liquors. The analysis in Table 124 is typical of this kind of water. The carbonate ratio is greater than 100, the difference between the quantity of carbonate ions and the calcium plus magnesium being accounted for by sodium. Sodium carbonate is consequently represented among the salts and the water may be referred to as "alkaline." The water is also shown as containing considerable quantities of sodium sulphate and chloride.

TABLE 124.—LONDON DEEP BORE WATER
 $(\text{Ca}^{++} + \text{Mg}^{++}) : \text{CO}_3'' = 100 : 124$

	Ions		Salts			
	Millivalls	Parts per 100,000		N/1000	Parts per 100,000	Grains per gallon
Sodium, $\text{Na}^+ \dots$	4.3	9.9	NaCl	1.7	9.9	6.9
Magnesium, Mg^{++}	1.6	1.9	Na_2SO_4	1.6	11.4	8.0
Calcium, $\text{Ca}^{++} \dots$	2.6	5.2	Na_2CO_3	1.0	5.3	3.7
Chloride, $\text{Cl}' \dots$	1.7	6.0	MgCO_3	1.6	6.7	4.7
Sulphate, $\text{SO}_4'' \dots$	1.6	7.7	CaCO_3	2.6	13.0	9.1
Carbonate, CO_3''	5.2	15.6	—	—	—	—
	—	46.3	—	—	46.3	32.4

(331) Type G. Pilsen Water.

Very soft liquor of the type used in the Pilsen breweries is regarded as the ideal for pale lager beers with delicate hop flavour. The analysis in Table 125 differs from all those previously given in its extreme softness. Soft waters of this type, with up to about 10 parts of solids per 100,000, are derived from the primary rocks or from surface supplies from the Millstone Grit and similar impervious formations. The carbonate ratio may vary considerably and in many cases is greater than 100 but the quantity of sodium making up the balance is too small to be significant in waters to which additions are made for brewing ales. Waters of this type provide the supplies of Liverpool, Manchester, Birmingham, Glasgow and other cities from lakes and catchment areas in mountainous districts. Many of the soft upland waters are brown, contain organic matter or acids and are not suitable for brewing unless purified by suitable treatment. The presence of iron is more than usually detrimental in the very pale lager beers for which these waters are used and means are adopted at Pilsen and elsewhere to remove any existing traces.

TABLE 125.—PILSEN WATER
(Ca⁺⁺ + Mg⁺⁺) : CO₃" = 100 : 71

	Ions		Salts			
	Millivalls	Parts per 100,000		N/1000	Parts per 100,000	Grains per gallon
Sodium, Na ⁺ ..	0·14	0·32	NaCl	0·14	0·82	0·57
Magnesium, Mg ⁺⁺ ..	0·07	0·08	MgSO ₄	0·07	0·42	0·29
Calcium, Ca ⁺⁺ ..	0·35	0·70	CaSO ₄	0·05	0·34	0·24
Chloride, Cl ['] ..	0·14	0·50	CaCO ₃	0·30	1·50	1·05
Sulphate, SO ₄ " ..	0·12	0·58	—	—	—	—
Carbonate, CO ₃ " ..	0·30	0·90	—	—	—	—
	—	3·08	—	—	3·08	2·15

(332) Types of Brewing Liquors.

Study of the analyses of the water supplies at some of the best known brewing centres and comparison with liquors used elsewhere for beers of similar character to those typical of these centres leads to a grouping such as that in Table 126.

TABLE 126.—CHARACTERISTICS OF BREWING LIQUORS

Saline composition	Special use	Typical locality
(1) HARD WATERS		
(A) <i>Very hard gypseous waters</i> . High proportion of Ca and SO ₄ , moderate quantity of Mg, comparatively small proportion of Na and CO ₃ .	Pale ale.	Burton-on-Trent.
(B) <i>Gypseous waters</i> . Generally not so hard as (A) with greater proportion of CO ₃ and Cl usually higher.	Pale lager and ales.	Dortmund.
(C) <i>Sulphate waters</i> . With still greater proportions of CO ₃ and increasing quantities of Na and Cl. Frequently characterised by the presence of sodium and magnesium sulphates in place of calcium sulphate.	Full-flavoured pale ales.	Edinburgh.
(D) <i>Carbonate waters</i> . Many city supplies fall in this group, Ca and CO ₃ predominant, with lower proportion of SO ₄ , moderate Na and Cl. Require treatment for pale ales after removal of carbonates.	Mild ales and stouts.	London (Metropolitan Water Board).
(E) <i>Carbonate waters</i> . Very small quantities of ions other than Ca, Mg and CO ₃ . Treatment for pale ales as (D).	Dark lager, stouts, mild ales.	Munich, Dublin.
(2) SOFT WATERS		
(F) Containing up to about 10 parts per 100,000 of total solids, with the individual ions in varying proportions corresponding with those found in hard waters. Very readily treated for ales.	Pale lager.	Pilsen.

REFERENCES

1. INTERNATIONAL SOCIETY OF MEDICAL HYDROLOGY, *International Register of Spas and Mineral Waters*. Headley Bros., London, 1931.
2. F. E. LOTT, *Journ. Inst. Brew.*, 1897, 3, 344.

CHAPTER XIX

LIQUOR COMPOSITION AND BEER CHARACTER

SALT EFFECTS

(333) Influence of the Liquor on Wort Composition.

The varying effects of different natural or treated liquors on the composition and properties of worts obtained by mashing the same malt in the same way can be shown by laboratory experiments. As an example some results obtained¹ by mashing 100 grams of the same pale English malt for 1 hour at 150° Fahr. with 400 ml. of each of 5 different natural waters, the volume of the mashies being finally made up to 500 ml., are given in Table 127. The liquors used in these experiments were :

- (1) Distilled water.
- (2) Carbonate liquor—A town supply containing 35 parts per 100,000 of solids, harder but otherwise similar in composition to that given in Table 122.
- (3) London deep well liquor—corresponding to that in Table 124.
- (4) Lichfield water—The town supply of Burton-on-Trent, somewhat similar to that of Dortmund, Table 120.
- (5) Burton-on-Trent bore water—Similar in type to that in Table 119, but containing 82 parts per 100,000 of total solids.

TABLE 127.—EFFECTS OF DIFFERENT NATURAL LIQUORS ON WORT COMPOSITION

	Distilled	Carbonate	London	Lichfield	Burton
Sp. gr. of water	1000.00	1000.44	1000.68	1000.49	1001.10
Extract Brs.' lb. per quarter	100.6	99.6	99.5	100.3	102.5
Colour, 1-in. cell Lovibond..	6.2	6.5	6.7	6.0	5.8
Dry solids, grm. 100 ml. ..	6.37	6.30	6.29	6.35	6.49
Perm. sol. nitrogen „ ..	0.427	0.422	0.415	0.451	0.500
Maltose (apparent) „ ..	3.89	3.93	3.89	3.91	4.05
p _H of water	6.8	7.4	7.8	7.5	7.2
p _H of wort	5.5	5.8	5.9	5.6	5.4

The most striking effects noted in experiments of this kind are (1) Variations in the extract obtained with the different liquors. In some cases it is greater than that obtained with distilled water,

in others it is less. It is not possible to make a direct correction for the specific gravity of the liquor when calculating the extract, because some of the salts which contribute to it are precipitated from the mash as carbonates or in combination with phosphoric acid from the malt, but it is apparent that carbonate and alkaline liquors give a lower extract than distilled water or gypseous liquors.

(2) The colour of the wort is less with gypseous than with carbonate or alkaline liquors.

(3) Considerable differences are observed in the break or flocculation when the worts are boiled. Gypseous waters give better flocculation and more brilliant worts than carbonate or alkaline liquors.

(4) The nitrogen content, in comparison with distilled water worts, is increased by using gypseous water and reduced by carbonates.

(5) Differences in the maltose content of the worts are usually insignificant, but may become considerable in presence of excess of carbonates.

(6) The hydrogen ion concentration or true acidity of the worts, as indicated by their p_H values, is affected differently by the liquors used. Gypseous waters increase the acidity, while carbonate and alkaline liquors reduce it, in comparison with the distilled water wort. These effects on the reaction of the wort are very significant, since most of the other differences found can be traced to the influence of the varying acidity of the mash on enzyme action or in other ways to be described later.

The differences in break, colour, extract and nitrogen content of the worts can be made more pronounced by mashing with solutions containing increasing weights of the various salts which may be supposed to exist in the liquors. The presence of greater quantities of sodium carbonate than can be assumed to occur in the alkaline London water, impedes filtration and makes it impossible to obtain a bright wort. A restrictive influence on the diastatic conversion of starch and production of maltose also becomes obvious with increasing carbonate alkalinity.

In practice the use of gypseous liquor or of carbonate water which has been treated by boiling to remove a large proportion of the carbonates and addition of gypsum or nearly neutralised with sulphuric acid, gives a paler wort from the same malt, more rapid filtration of the mash, better break in the copper and a greater yeast growth than untreated carbonate liquor. The greater yeast growth is probably attributable to the increased nitrogen content and amino-nitrogen content of the wort.

Varying proportions of gypsum and carbonates have similar effects in decoction mashes, as shown in Table 129 by Moufang.²

A pale lager malt was used in each case and mashed with distilled water in which the salts typical of Munich, Vienna, Pilsen and Dortmund had been dissolved. Mashers were made with and without a protein rest, so that they also show the effect of this factor.

TABLE 128.—COMPOSITION OF LIQUORS USED IN EXPERIMENTAL BREWS
(PARTS PER 100,000)

	Munich	Vienna	Pilsen	Dortmund
Calcium sulphate	1.0	30.7	28.2	40.0
Magnesium sulphate ..	—	—	3.0	—
Calcium chloride	—	—	—	12.5
Magnesium chloride ..	—	2.4	—	1.3
Calcium bicarbonate ..	30.7	30.4	—	18.0
Magnesium bicarbonate ..	10.6	20.0	6.1	—
Sodium chloride	0.5	3.4	6.6	6.1

The different waters produced striking differences in the rate of saccharification, filtration of the mash, extract, acidity and final attenuation. The records of flavour and character indicate that the beers from the carbonate liquors, typical of Munich and Vienna, were quite different from the others and, although made from a pale malt, they possessed much of the character of Munich beers. Very similar results are obtained with an infusion mash and top fermentation and they correspond with the tendencies noted in practice with waters of the types exemplified.

TABLE 129.—INFLUENCE OF LIQUOR ON WORT COMPOSITION AND CHARACTER
WITH AND WITHOUT PROTEIN REST (A) AND (B)

	Munich		Vienna		Pilsen		Dortmund	
	A	B	A	B	A	B	A	B
Saccharification, minutes ..	75	70	60	60	15	15	10	10
Drainage rate, comparative ..	28	40	21	26	8	7	8	8
Aroma of wort	strongly aromatic		aromatic		neutral		neutral	
Colour of wort65 dark brown, red		.48 less red		.35 pale yellow		.29 pale greenish	
Extract % on dry malt ..	76.5	76.1	77.2	76.6	78.5	77.7	78.3	77.1
Acidity, wort % lactic acid ..	.084	.070	.067	.066	.137	.121	.121	.105
„ beer „ „ ..	.121	.102	.097	.092	.175	.168	.207	.150
Nitrogen % in 10% wort ..	0.066	0.064	0.066	0.065	0.071	0.070	0.074	0.071
% of nitrogen assimilated ..	32.0	—	30.0	—	28.0	—	25.0	—
Final attenuation	71.4	68.1	71.8	69.4	75.8	73.9	77.4	75.8

(334) Reaction of a Malt Mash.

Mashing is a process in which the starch and other constituents of the malt are converted to simpler soluble substances by a number of enzymes, which depend for the exercise of their greatest activity not only on the temperature of the mash but also on its reaction or acidity. The most favourable reaction for starch conversion in the mash tun is generally at a p_H value of about 5.1 in ale brewing but may be somewhat higher for lager beer. If the acidity of the mash is less than is indicated by this figure, that is if the p_H value is higher than 5.1, the activity of diastase or starch conversion is restricted just as it would be by raising the temperature. It is consequently of advantage to regulate the p_H value of the mash to 5.1, or to 5.4 or a slightly higher value in some cases for lager beer in accordance with the desired enzymic activity. Further, it may be noted that the activity of the proteolytic enzymes is greatest at an even more acid reaction, represented by p_H values below 5.0.

An infusion of malt in distilled water exhibits an alkaline reaction to methyl-orange but appears to be acid if tested with phenol-phthalein. That is to say its p_H value lies somewhere between 4.2 and 9.0, at which these two indicators respectively change colour. More accurate measurements show that the p_H value is usually between 5.5 and 6.0 with ale malts and between 6.0 and 6.5 with lager malts. In any case the reaction of the mash is more alkaline than is required for the most energetic enzyme action. This was demonstrated in the simple mashing experiments with different waters already described. These showed that some waters containing gypsum reduced the p_H value of the mash, that is increased its acidity, and that the p_H value was increased, or acidity reduced, if the malt was mashed with water containing carbonates. The result of an increase in acidity was a greater extract and more nitrogen dissolved in the wort, due to activation of diastase and proteolytic enzymes. On the other hand the carbonates restricted the enzymic changes. The experiments show that these salts have the very important property of changing the reaction of the mash to the advantage or disadvantage of enzymic conversion respectively. The salts may have significant effects on flavour and other properties of the beer but this influence on enzymic action is so important and well marked that it has provided the basis for modern methods of liquor treatment. It is the only aspect of liquor influences that can at present be explained adequately.

(335) Phosphate Reactions in the Mash Tun.

The p_H value of a malt mash in distilled water depends on the substances extracted from the malt. These comprise a number of buffer systems, including protein degradation products, weak organic acids with their salts and primary and secondary phosphates in varying proportions. The phosphates of potassium are the most important mineral constituents of malt, and Fernbach showed that the p_H value of wort was largely dependent on their relative proportions. Dilute solutions of the primary potassium phosphate, KH_2PO_4 , have an acid reaction, with a p_H value about 5.0, while solutions of the secondary salt, K_2HPO_4 , are slightly alkaline, p_H 9.2. Together they form a buffer mixture with p_H value depending on their relative proportions. This must be higher than p_H 5.0, so that mixtures in natural organic liquids prevent diastatic, proteolytic and other enzymes from exerting their greatest activity. The action of the enzymes is consequently increased by neutralising the alkalinity of the secondary phosphate as was shown by Fernbach and Hubert.³ This can be effected by any reaction which converts secondary potassium phosphate into the primary phosphate or by precipitating some of the P_2O_5 in such a way that the proportion of primary phosphate left is increased. The reverse reaction, involving conversion of primary to secondary phosphate or reduction of the proportion of primary phosphate by precipitation or otherwise, increases the alkalinity of the mixture.

The explanation of the influences of gypsum and carbonates on the reaction of the mash is based on the behaviour of these salts with mixtures of the phosphates. Malts usually contain slightly less than 1% of P_2O_5 , of which about one-fifth exists in a soluble form, while a further 50 or 60% of the total becomes soluble during mashing, mainly as potassium phosphates, of which about one-tenth may be secondary potassium phosphate and the remainder the acid primary salt. Many attempts have been made to relate the p_H of the mash and wort to reactions between the malt phosphates and liquor salts. An example of the results of such an investigation by Siegfried⁴ is given in Table 130. The figures represent analyses of worts obtained by mashing 75 grams of English malt with distilled water and with dilute solutions of various salts. The mashes were finally made up to 450 grams, giving worts with specific gravities of approximately 1048. The composition of the ash of wort made with distilled water varies considerably with different malts. In the present example the calcium is rather less than usual and the magnesium content rather greater. The salt additions are given at the foot of the table.

TABLE 130.—ANALYSES OF THE ASH OF MALT AND OF WORT

Liquor, gr. per 100 ml.			Sp. gr. wort	Gram per 100 m.l. wort					p_H wort
CaO	MgO	SO ₃		Ash	SO ₃	P ₂ O ₅	CaO	MgO	
Distilled			1048-13	0-208	0-0146	0-1015	0-0047	0-0217	5-37
A. (1) 0-0057	—	—	1048-02	0-189	0-0149	0-0858	0-0065	0-0190	5-61
(2) 0-0120	—	—	1047-81	0-174	0-0147	0-0764	0-0073	0-0162	5-68
(3) 0-0281	—	—	1047-60	0-159	0-0149	0-0581	0-0107	0-0122	5-95
B. (1) 0-0068	—	0-0095	1048-44	0-199	0-0252	0-0923	0-0075	0-0204	5-37
(2) 0-0127	—	0-0181	1048-41	0-187	0-0337	0-0851	0-0104	0-0202	5-25
(3) 0-0245	—	0-0351	1048-93	0-193	0-0506	0-0794	0-0154	0-0204	5-14
C. (1) —	0-0039	—	1048-11	0-193	0-0155	0-0889	0-0047	0-0225	5-58
(2) —	0-0079	—	1048-11	0-180	0-0151	0-0801	0-0033	0-0217	5-66
(3) —	0-0157	—	1047-76	0-162	0-0157	0-0662	0-0028	0-0227	6-03
D. (1) 0-0276	—	0-0271	1048-52	0-184	0-0444	0-0732	0-0157	0-0186	5-34
(2) 0-0259	—	0-0192	1048-31	0-171	0-0363	0-0674	0-0137	0-0164	5-46
(3) 0-0278	—	0-0100	1048-11	0-162	0-0266	0-0630	0-0124	0-0144	5-82
Analysis of malt, per cent.	..	—	—	2-07	0-107	0-853	0-080	0-211	
Ash of wort, % on malt..	..	—	—	1-15	0-081	0-560	0-026	0-120	

SALTS ADDED TO THE MASHING LIQUORS

	Parts per 100,000 of liquor			Milligram-equivalents per litre		
	1	2	3	1	2	3
(A) Calcium bicarbonate	16-5	34-7	81-3	2-03	4-28	10-03
(B) Calcium sulphate	16-3	30-8	59-6	2-40	4-53	8-75
(C) Magnesium bicarbonate	14-2	28-8	57-3	1-94	3-94	7-85
(D) Calcium sulphate	46-1	32-6	17-0	6-78	4-80	2-50
Calcium bicarbonate	24-5	36-5	60-2	3-02	4-50	7-43

Examination of the figures in Table 130 shows that the p_H of the wort rises with increasing additions of calcium or magnesium carbonates and that its acidity is increased by gypsum additions. In every case the total ash of the worts made with treated liquors is less than that of the distilled water wort, but it does not appear possible to find any definite relation between the quantities of P₂O₅, CaO and MgO precipitated and those of the carbonates or gypsum added. This is more clearly shown by the figures in Table 131, which represent the quantities added and precipitated in milligram-equivalents per litre. It appears that the precipitating effect of gypsum is only about half that of calcium bicarbonate and about two-thirds of that of magnesium bicarbonate and that complicating influences exist when mixtures of calcium bicarbonate and sulphate are added. In all cases the quantity of

sulphate in the wort corresponds with that derived from the malt together with that in the liquor.

TABLE 131.—PRECIPITATING EFFECT OF EQUIVALENT QUANTITIES OF SALTS

Additions, millivals					Precipitated, millivals		
	Ca ⁺⁺	Mg ⁺⁺	CO ₃ ⁼⁼	SO ₄ ⁼⁼	PO ₄ ^{'''}	Ca ⁺⁺	Mg ⁺⁺
A (1) ..	2.0	—	2.0	—	6.6	1.4	1.3
(2) ..	4.3	—	4.3	—	10.6	3.4	2.7
(3) ..	10.4	—	10.4	—	18.3	7.9	4.7
B (1) ..	2.4	—	—	2.4	3.9	1.4	0.6
(2) ..	4.5	—	—	4.5	6.9	2.6	0.7
(3) ..	8.7	—	—	8.7	9.3	5.1	0.6
C (1) ..	—	1.9	1.9	—	5.3	—	1.5
(2) ..	—	3.9	3.9	—	9.0	0.5	3.9
(3) ..	—	7.8	7.8	—	14.9	0.7	7.3
D (1) ..	9.8	—	3.0	6.8	11.9	5.9	1.5
(2) ..	9.3	—	4.5	4.8	14.4	6.0	2.6
(3) ..	9.9	—	7.4	2.5	16.2	7.2	3.6
In distilled water wort					42.8	1.7	10.8

Since the reactions described all result in precipitation of calcium or magnesium phosphates, it is to be expected that relatively high quantities of those salts would be found in the grains when hard waters were used for mashing. The effect of this is shown in Siegfried's analyses of the ash of washed grains from infusion mashes, Table 132.

TABLE 132.—ASH OF SPENT GRAINS

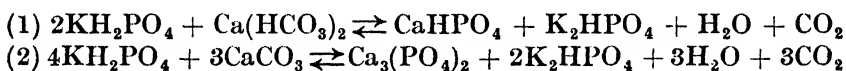
Water	Hardness as CaCO ₃ pts. per 100,000	Per cent. on dry matter of Grains				
		Ash	CaO	MgO	P ₂ O ₅	SO ₃
Distilled ..	0	3.13	0.136	0.235	0.506	0.064
Ca(HCO ₃) ₂ ..	49.0	4.79	0.669	0.481	1.586	0.056
CaSO ₄ ..	49.9	3.80	0.535	0.235	1.022	0.058
Mg(HCO ₃) ₂ ..	40.2	4.29	0.286	0.581	1.305	0.055

(336) Effect of Phosphate Reactions on the p_H of the Mash.

The results of the experiments described and of others carried out in a similar manner show that it is impossible to construct equations to represent quantitatively the behaviour of the phosphates in the mash tun. It is, however, permissible to base a generalised explanation of the influence of certain salt additions

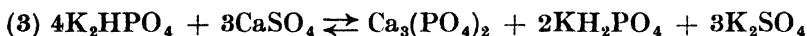
on the reaction of the mash on the chemical exchanges which occur when these are mixed with phosphate solutions. It must be noted that all the equations given with this object represent balanced reactions which come to different equilibria according to the existing conditions of temperature and concentration or in presence of other substances which may tend either to complete the reaction or prevent it. Precipitation of phosphates occurs to a certain extent in all these reactions, the quantities precipitated varying with the solubility of the different calcium and magnesium phosphates under the existing conditions. Primary calcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, is fairly readily soluble in water; secondary calcium phosphate, CaHPO_4 , is slightly soluble and largely precipitated, while tertiary calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ is insoluble and precipitated. The corresponding magnesium salts are more soluble than those of calcium. The potassium salts are all readily soluble. Since the primary salts are more acid than the secondary, any reaction which causes a reduction in the proportion of the former or increases that of the latter reduces the acidity of the solution or wort and *vice versa*. The reactions illustrated are consequently divided into two groups, according to their influence on the acidity of the wort.

(a) *Resulting in reduction of acidity*, reactions with carbonates.



The second equation might represent the reaction with waters containing greater quantities of calcium carbonate. It should be noted that reduction of acidity is brought about in two ways. (1) By conversion of the primary salt to secondary, completely or in part, and (2) by removal of some of the phosphate ions by precipitation as insoluble tertiary salt. The primary phosphates are acid salts and the secondary react as basic salts with salts of stronger acids.

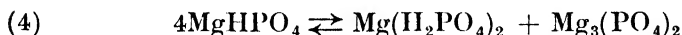
(b) *Resulting in increase of acidity*, reaction with gypsum.



In this case the alkalinity produced by the secondary potassium phosphate is in part removed by precipitation of tertiary calcium phosphate and partly by transformation to the acid salt. The potassium sulphate has no effect on the acidity. It will be noticed that gypsum tends to counterbalance the alkalinity-producing effect of calcium carbonate. The quantity required to produce maximum acidity must therefore depend not only on the amount of

secondary phosphate present, that is on the quantity of the malt, but also on the carbonate content of the liquor.

The presence of magnesium salts in the water complicates the chemical changes considerably, on account of the greater solubility of the magnesium phosphates and exchanges with calcium. As magnesium is almost always present in smaller quantity than calcium, the reaction with magnesium carbonate tends, according to Windisch, to follow the course represented by equation (1) rather than (2). The secondary magnesium phosphate is soluble and raises the alkalinity of the wort. Magnesium carbonate also makes water more alkaline than an equivalent quantity of calcium carbonate. Secondary magnesium phosphate is unstable when its aqueous solution is heated and changes to a mixture of tertiary phosphate, which is precipitated, and primary phosphate which increases the acidity of the solution. On cooling the reaction is reversible and the solution becomes more alkaline again.



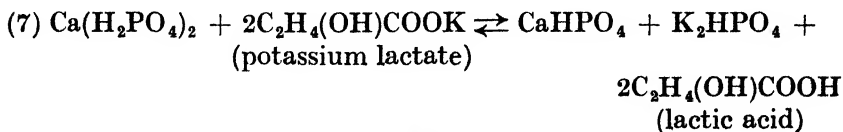
Further, gypsum reacts with MgHPO_4 , precipitating CaHPO_4 , but the change is by no means quantitative.



Sodium and potassium carbonates have a much greater effect on the reaction of the mash and wort than calcium and magnesium carbonates, because the secondary phosphates formed from primary phosphate are soluble and alkaline.



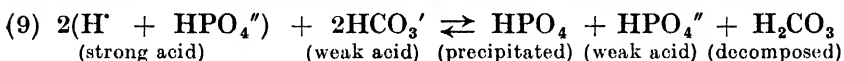
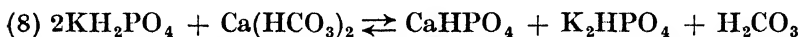
Among other constituents of the malt which have an influence on the reaction of the mash are salts of weak organic acids and amino-acids. The neutralisation of carbonates by free organic acids, particularly in such materials as Enzymic malt, is a case in which the hydrogen ion concentration of the mash may be materially increased, but there are possibilities that some of the salts may have an opposite influence. The salts of weak organic acids are hydrolysed, particularly at high temperatures, forming undissociated acids and strongly alkaline bases. They may also act in the manner represented in equation (7) in presence of phosphates.



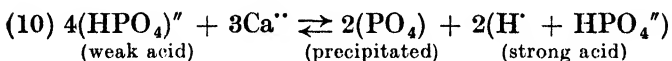
(337) Effects of Ions in Brewing Liquor.

If these reactions are referred to the ions, it will be observed that only four of those commonly occurring in water are able to modify the equilibrium among the phosphates derived from malt. These are CO_3'' , HCO_3' , Ca'' and Mg'' . Explanation of any effects produced by Na' , K' , SO_4'' , Cl' or NO_3' must be sought in other directions.

CO_3'' and HCO_3' decrease acidity or increase alkalinity, because carbonic acid is a weaker acid than phosphoric and in its presence the dissociation of the stronger acid is decreased. Carbonates diminish the number of H ions liberated in this dissociation and consequently the true acidity of the liquid. That is to say a weak acid acts as a base in presence of a stronger acid, as is represented in equations (8) and (9). In the second equation the acids only are represented and it should be noted that the weak acids are practically undissociated, or ionised to a smaller extent.



The increase in acidity in presence of gypsum and, to a smaller extent, in presence of magnesium sulphate, is due to the action of the calcium and magnesium ions, as shown in equation (10) derived from equation (3). The ions concerned in the change in reaction are given in (10).



In this respect magnesium is less efficient than calcium on account of the greater solubility of its phosphates.

In the absence of carbonates, the acidifying action of calcium ions is limited by the amount of secondary phosphates present, but, as already noted, a considerable excess of calcium would in most cases be required to bring the changes to the final state represented by the equation. The action of acidifying and acid-reducing ions is, however, additive and, since CO_3'' is twice as active in reducing acidity as calcium is in increasing it, allowance must be made for any carbonates present.

This additive relation also explains the very harmful effect of sodium carbonate in brewing liquor. In this case the acid-reducing effect of the CO_3'' is not counterbalanced at all, as the sodium ion is inactive, and there is no precipitation of tertiary phosphate. Sodium carbonate has therefore a greater retarding effect on the activity of enzymes than has an equivalent quantity of calcium carbonate.

This rule for the individual ions of a salt may be applied to the mixture of ions present in brewing liquor and hence the effect of the liquor on the reaction of the mash can be deduced by comparing the quantity of calcium and magnesium ions with those of CO_3 . The unit for comparisons of this sort is the millival and not the actual weights of calcium, magnesium and carbonate present, which are not in proportion with their equivalent weights. 20 parts per 100,000 of calcium is equivalent to 30 parts per 100,000 of CO_3 or 61 of HCO_3' but 20 parts per 100,000 of calcium or 10 millivals are required to produce as much primary phosphate from secondary as 15 parts per 100,000 or 5 millivals of CO_3 convert to secondary.

(338) Buffer Action of Bicarbonates.

The foregoing manner of regarding the phosphate reactions has emphasised the buffer effect of a mixture of primary and secondary phosphates, the one resisting the action of bases, the other of acids. There is in addition the buffer action of the bicarbonates themselves, which keeps the p_{H} of most waters somewhere between neutrality and p_{H} 7.5 and resists the acidifying effect of hydrogen ions. Regarded in this light, equation (9) expresses the buffering action of HCO_3' against the hydrogen ions liberated from CaH_2PO_4 , thus



The result is the same, a reduction of hydrogen ion concentration. This reaction also explains why addition of a strong acid, such as sulphuric, to a carbonate water only produces a very gradual change in p_{H} value until the bicarbonate is completely decomposed, after which there is an immediate and great decrease in p_{H} .

INFLUENCE OF THE LIQUOR ON THE CHARACTER OF BEER

(339) Influence on Flavour.

Every water capable of increasing the acidity of the mash and wort is not necessarily a good brewing liquor, neither can any one liquor be expected to be suitable for all types of beer. Requirements vary greatly, as is clearly shown by the use of carbonate liquors for the dark aromatic lagers of Munich, for Dublin stouts and for dark, lightly hopped mild ales in general, while a strongly gypseous liquor appears to be the best for pale ales and a soft water for Pilsen lagers. The most advantageous hydrogen ion concentration in mash and wort varies with the materials, the method of mashing, the hop rate and beer character desired.

A carbonate liquor gives an abnormal colour to pale wort and darkens the beer. The pure yellow, sometimes shading to a faintly greenish yellow, of very pale lager beers is changed to a reddish tinge. A gypseous liquor reduces the colour of beers materially.

The effect of carbonates is particularly marked in respect of hop flavour. It is a common saying that carbonate waters are hop savers, while soft waters are hop wasters in view of the extra bitterness brought out by the former with the same hop rate. The character of the hop bitter is, however, adversely affected as well as increased in intensity by the carbonates. It becomes harsh and clinging, for which reason the carbonate liquors are unsuitable for generously hopped bitter beers, though they may be useful for more lightly hopped and sweeter beers in which the harshness cannot become so pronounced. Liquors with an original calcium carbonate content of up to about 20 parts per 100,000 are widely used for such beers. It is difficult to relate the quantity of carbonates to flavour on account of the readiness with which a large proportion is removed by boiling before it can influence the composition of the wort. Their deleterious influence on hop flavour is due to alkalinity, and reduction of the p_H of the wort by gypsum has much to do with the cleaner hop flavour produced in its presence. Gypseous waters permit of the use of a considerably higher hop rate than is possible with carbonate liquors, and of a greater proportion of such strongly flavoured hops as Oregon Clusters without fear of objectionable harshness.

The influence of the carbonates, gypsum and other salts on flavour is due not only to differences in the hop extraction. The salts themselves are more or less bitter and, in addition, influence the flavour of beer by their varying effects on protein precipitation. Gypsum assists coagulation during boiling and cooling and brings a cleaner wort to the fermenting vessel than carbonate liquors. With these, colloidal particles with adsorbed hop resins remain in a state of fine division and pass to the fermenting vessels, where some of the resins are dissolved in the wort. Although it is found in practice that a reduction in p_H value is favourable to precipitation and removal of proteins during boiling and cooling, their extraction and dispersion are also influenced by the ions of the salts. A complete explanation of the effects of different liquors on copper break, wort clarification and flavour cannot be based on the p_H values alone, but must be sought also in other aspects of the general properties of colloids.

(340) Gypsum Requirements.

It will be recognised that reactions between calcium and

magnesium ions of the liquor and phosphates of the malt only constitute one factor among a number that may influence the hydrogen ion concentration of the mash and wort. The buffer action of the phosphates only appears to be effective over a range of p_H values between 5.7 and 7.0 (Hopkins and Kelly⁵), although the influence of gypsum additions extends below p_H 5.7. The amino-acids and peptones are operative as buffers from p_H 5.7 to p_H 3.7. Reactions between calcium or magnesium and organic acids derived from the malt must also be taken into account, while a certain quantity of carbonates remains in solution in the wort, increasing the alkalinity. The problem is thus very complicated but the phosphate exchanges appear to offer the most satisfactory theoretical guide yet available on the behaviour of different mashing liquors.

The important question as to how much gypsum should be present in mashing liquor is answered in various ways by brewers of different types of beer. The brewer of pale lager holds that any benefits that might accrue from increase of acidity are more than offset by its deleterious effects on flavour. He obtains the necessary adjustment of p_H by removal of carbonates. The pale ale brewer, who requires a lower p_H in the mash, usually pays less attention to the carbonates but counterbalances their ill effects by generous gypsum additions, fearing no depreciation of flavour in the infusion mash. The best guide for an ale liquor would appear to depend on measurements of the change in the p_H value of the worts produced by increasing gypsum additions, under the conditions existing in the particular brewery.

The quantity of phosphoric acid derived from malt and dissolved in the wort is very considerable, amounting to about 2 lb. of P_2O_5 per quarter, while the mineral matter in 2 barrels of liquor containing 100 grains per gallon would be little more than 1 lb. If the secondary phosphates are placed at as low a figure as one-tenth of the primary, the malt might yield about 0.06% of its weight as secondary phosphates. About 28 grains per gallon of gypsum in mashing liquor used at the rate of 2 barrels per quarter or 19 grains per gallon if used at the rate of 3 barrels per quarter would apparently suffice to convert all this to primary phosphate and tertiary calcium phosphate if equation (3) actually represented the reaction. Hagues⁶ found in some experimental mashes with English malt at the standard rate for extract determination that 21 grains per gallon of $CaSO_4$ produced the maximum increase in acidity, from p_H 5.8 to p_H 5.6. As the specific gravity of the worts was only about 1029, it would appear that 42 grains per gallon would have been required under similar conditions for worts of 1058.

The beneficial influence of gypsum on the p_H of the mash is apparently limited by the quantity of secondary phosphate present, but other factors must be taken into consideration. A certain quantity is required to counterbalance the opposing effects of carbonates. The results in Table 130 show an increase in acidity with 21 grains per gallon of gypsum in absence of carbonates with wort of 1048 sp. gr. and that 32 grains per gallon is just sufficient in presence of 17 grains per gallon of calcium bicarbonate. It may be deduced from the figures for added salts, that rather more than two equivalents of gypsum (136 parts by weight) are required to counterbalance one equivalent of calcium bicarbonate or carbonate (81 or 50 parts by weight). In practice a slight increase in acidity may be expected when the quantity of gypsum present in the liquor is about twice that of the carbonates but there is generally a reduction in the acidity of the mash when they are present in equal quantities. Moderate gypsum additions in liquor treatment often cause no increase in the calcium content of the wort, though all the sulphate added will be found in solution.

Calcium chloride added to brewing liquors has a similar effect to that of gypsum on the acidity of the mash, in as much as this is due to the calcium ions, but its influence on flavour is different. This is on account of the chlorine ions which tend to increase the fulness of beer but increase the hop bitter.

(341) Magnesium Salts.

The greater solubility of the magnesium phosphates and carbonate in comparison with the calcium salts causes magnesium bicarbonate to reduce the acidity of the mash to a greater degree than an equivalent quantity of the calcium salt. The difference of opinion between ale and lager brewers in regard to the usefulness of magnesium salts is as marked as that in respect of gypsum. The former generally hold that magnesium sulphate is among the essential nutrients of yeast and most liquor treatments contain a proportion of this salt, unless the water analysis shows a larger quantity of magnesium than is usual. Lager brewers generally dread the presence of magnesium salts in any form, on account of the greater difficulty of softening waters in which they occur and because magnesium phosphates are more soluble than the corresponding calcium salts and only very incompletely precipitated in the mash. They thus interfere with the desired reduction in p_H of the wort and do not reduce its buffer content or resistance to the acidifying action of yeast during fermentation. Further, magnesium sulphate has a bitter flavour which may be unpleasant if detectable and its physiological effects are well known,

though unlikely to be experienced in other than a beneficial form at such low concentrations as occur in natural brewing waters.

Both these views are probably exaggerated. The quantity of magnesium contained in malt, yielding 10 to 20 parts of MgO per 100,000 of wort of 1050 sp. gr., should be sufficient for the nutritional requirements of yeast, but very little information is available on the minimum required by the yeast or the maximum permissible to avoid detrimental effects. In this respect liquor treatment is almost entirely based on hypothetical considerations or on empiricism. Siegfried's fermentation experiments with the worts of Table 130 showed a decrease of mineral matter due to assimilation by the yeast and, to a certain extent, on account of precipitation. There was a small decrease, amounting to about 8%, in the SO_3 content of these worts but 20% of the P_2O_5 was removed during fermentation. The magnesium content of the worts fell in most cases by between 5 and 8%, suggesting that magnesium is a useful yeast nutrient, but the quantity assimilated hardly supports the contention that it is necessary to add more magnesium sulphate to that already present in the wort and derived from the malt.

(342) Buffering of Wort.

TABLE 133.—INFLUENCE OF CARBONATES AND SULPHATES ON THE BUFFERING OF WORT

	P_2O_5 grams per 100 ml.	p_{H}	Titration ml. per 100 ml. wort			
			N/10 NaOH neutral red	N/10 NaOH phenol- phthalein	N/10 HCl methyl- orange	Buffers p_{H} 7-4.2
Distilled water	0.05030	6.45	2.5	18.0	5.0	7.5
+ 35.7 pts. 100,000 CaCO_3	0.03297	6.90	0.8	17.0	8.0	8.8
+ 30 " " MgCO_3	0.04130	6.90	0.8	17.0	7.0	7.8
+ 36.4 " " CaSO_4	0.04868	6.16	2.0	19.0	4.5	7.5

Gypseous liquors reduce the buffering of wort by removal of secondary phosphates. As a result the wort offers less resistance to the natural increase of acidity during fermentation and gives beers with a lower p_{H} value at racking than worts made with soft water or, still more, with carbonate liquors which increase the buffering. The beneficial effects of calcium sulphate on the acidity of the mash are not shared equally by magnesium sulphate, on account of the greater solubility of the magnesium phosphates and a further result of this solubility is that the buffering power of the wort is not reduced to the same extent by magnesium sulphate

as by gypsum. An example, by Lüers and Nishimura,⁷ of the influence of sulphates and carbonates on the buffers of wort is given in Table 133. In these experiments gypsum had no effect on the buffering between p_H 7 and 4.2 of a wort made from a pale lager malt by the Congress method of mashing. Calcium carbonate increased the buffering quite considerably but the effect of magnesium carbonate was less marked.

(343) Influence of the Liquor on Enzyme Action.

One of the most important effects of variations in the p_H of the mash caused by different liquors is that on enzyme activity. The differences in extract, permanently soluble nitrogen and maltose content shown in Tables 127 and 129 are due to this. More detailed analyses reveal other variations in wort composition, such as in respect of its amino-nitrogen content, all of which can be traced to increased or decreased enzymic breakdown of starch, protein or other malt constituents. The enzymes concerned are most active at different p_H values ranging slightly above and below p_H 5.0, which is well below that of a mash made with distilled water. The action of gypsum, which brings the p_H value down towards the optima of the enzymes, is consequently favourable to their activity, while carbonates, which reduce the acidity of the mash, are restrictive. The influence on diastatic conversion of starch within the range of acidity affected by the liquor is quite significant, but the activating effect of increased acidity is considerably more marked in respect of the proteolytic enzymes.

In this, as in all other examples of liquor influences traceable to changes in p_H value, consideration must be given to the malt as well as the water. The actual reaction obtained depends also on the composition and acidity of the malt and may be varied to some extent by the conditions of mashing. The nature of the liquor is thus only one, but an important, factor in wort composition and beer character.

The effects on extract are complicated by the specific gravity due to the added salts. A correction cannot, however, be made merely by deducting the specific gravity of the liquor from that of the wort, on account of the precipitation of phosphates, but an approximate correction can be made for the ash of the wort by use of the solution divisor 8.0, as has been done in Table 134. An increase in extract due to organic matter is then shown in the presence of gypsum, while carbonates cause a definite reduction. The figures also show the variations with different malts, in this case English malts mashed by the Institute of Brewing method, giving approximately 10% worts, with waters containing 12 to 114 parts per 100,000 of gypsum.

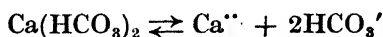
TABLE 134.—REACTIONS BETWEEN GYPSUM IN LIQUOR AND PHOSPHATES OF MALT AND THE EFFECT ON EXTRACT

Liquor, g. per 100 ml.			Extract		Grams per 100 ml.					
					Wort			Boiled wort		
CaSO ₄	CaO	SO ₃	lb. per quarter dry	Corrected for ash	Ash	P ₂ O ₅	CaO	SO ₃	P ₂ O ₅	% P ₂ O ₅ pptd.
MALT A										
—	—	—	98.7	95.1	.1330	.066	.0060	.0172	0.063	4.5
.012	.0049	.0071	99.1	95.4	.1320	.064	.0080	.0237	0.058	12.1
.024	.0099	.0141	99.3	95.8	.1330	.059	.0124	.0308	0.055	16.6
.048	.0198	.0282	99.9	96.1	.1410	.055	.0186	.0449	0.052	21.2
MALT B										
—	—	—	100.3	96.6	.1384	.070	—	—	.068	2.9
.038	.0156	.0224	101.6	97.7	.1482	.063	—	—	.059	15.7
.076	.0313	.0447	102.5	98.0	.1670	.056	—	—	.054	22.9
.114	.0470	.0670	103.4	98.1	.1966	.054	—	—	.050	28.6

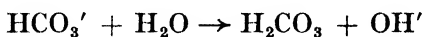
(344) Salts in Sparge Liquor.

The conditions obtaining during sparging are different from those during the earlier part of the mashing process, particularly in the later stages of sparging when the soluble and converted substances have been to a large extent removed from the grains. Enzymic action then comes practically to an end and the extraction which still takes place to a small extent depends greatly on the physical action of large volumes of hotter liquor on refractory carbohydrate and protein material. These exist in a colloidal state in the grains and their peptisation and extraction is facilitated by use of an alkaline liquor. At this stage the alkalinity of carbonates in the liquor receives little check from phosphates and organic buffers, which are more and more completely removed from the mash tun as sparging proceeds. As will be shown in a later chapter, the substances extracted become more and more detrimental to the quality of the wort. It is therefore essential that a carbonate liquor should not be used for sparging, when its own alkalinity becomes the predominant factor in the reaction. Very little is known of the effects of other salts during sparging, but increasing alkalinity will be shown later to have a very definite influence on the composition of the wort in directions which practical experience has found lead to difficulties in respect of brilliance and stability in the beer. It was shown that the alkalinity of a carbonate water is due to dissociation of the bicarbonate ion and liberation of OH' ions from water. All reactions attributed to carbonates should be referred to the bicarbonate ions, since the salts exist

as bicarbonates which are dissociated to give the bicarbonate ion,



The bicarbonate ion then reacts with water to give carbonic acid, which decomposes to H_2O and CO_2 but leaves the hydroxyl ion to produce alkalinity or increase the p_{H} of the liquid,



(345) Salts of the Alkali Metals.

The carbonates of potassium and sodium can be shown by mashing and boiling experiments to have an even more detrimental effect on the colloidal composition of wort and on the hop flavour of beer than the corresponding calcium and magnesium salts. Apart from these, the salts of the alkali metals, with the possible exception of the silicates, have no influence on the p_{H} value of the wort. Definite information on the behaviour of the small quantity of silica or silicates almost invariably present in water is lacking but it is probably unfavourable, in so far as the silica may form colloidal complexes or reduce the acidity of the mash. It may, however, be mainly precipitated as silica and have no further influence on the wort or beer.

Potassium rarely occurs in more than very small quantity in natural brewing waters and its effects are probably similar to those of sodium. Its salts are among those made use of in mineral culture solutions and it is possible that the small quantity present in some brewing liquors is of physiological importance for the yeast. Potassium sulphate and chloride are used for this reason in many liquor treatments.

The chloride and sulphate of sodium, and less frequently of potassium, are the most commonly occurring salts of the alkali metals. Sodium sulphate is generally believed to give a tendency to harsh, hard flavours but many liquors used with success in ale brewing apparently contain a moderate amount of this salt or of the ions derived from it. Common salt, if present in or added to the liquor in any considerable quantity, increases the fulness of mild ales but gives an unpleasant bitter with pale, generously hopped beers. A balance may thus be arrived at between a desirable increase in fulness and an unpleasant bitter flavour, varying with the materials used, the gravity of the wort and other constituents of the liquor. For top fermentation beers with moderately hard liquors, 10 parts per 100,000 of sodium chloride may generally be found desirable, with quantities ranging through 20 to 30 parts per 100,000 for mild ales and up to as much as 50 parts per 100,000 for full-flavoured dark ales

or stouts. Quantities in excess of this are liable to interfere with fermentation.

Nitrates usually occur only in very small quantity in brewing liquors. They are generally held to be detrimental to the health of yeast, whether existing in the form of salts of the alkali or alkaline earth metals. Experiments have been recorded by W. and F. Windisch,⁸ with 1.7, 4.3 and 17 parts per 100,000 of NO_3 in which it was found that the added nitrate had no appreciable influence on the attenuation in bottom fermentations during the first two or three days but, afterwards, their deleterious influence became more and more marked. With top fermentations the effects were pronounced in 16 to 18 hours owing to the higher temperatures. The poisonous effect is ascribed to reduction of nitrates to nitrites, or of NO_3 to NO_2 . No practicable method for removing nitrates from brewing waters exists and liquors containing more than 3.5 to 5 parts per 100,000 of NO_3 should be regarded with suspicion, although many hard waters containing appreciably more are used with success. The yeast, however, frequently takes on a more or less oval shape after a few generations in worts brewed from liquors containing 5 to 10 parts per 100,000. The safest course to pursue when such liquors must be used is to obtain a change of yeast as soon as deterioration or defects in fermentation become apparent.

(346) Physiological Effects of the Salts.

Apart from their influence on flavour, the salts have a considerable influence on the physiological effects of beer as a beverage. A certain quantity of salts is essential in a thirst-quenching beverage to replace those secreted from the body in perspiration. To these the salts in the liquor, particularly sodium chloride, must contribute, as well as those extracted from the malt, but it is not possible to specify desirable quantities. The calcium and magnesium salts, whether derived from the liquor or the malt, and the important quantities of potassium and phosphates from the latter no doubt contribute helpfully to the mineral nutritional requirements of the human body, as they so definitely do to those of yeast.

CLASSIFICATION OF BREWING LIQUORS

(347) Carbonate Ratio.

Variations in the total quantity of salts dissolved in the liquor have a most important influence on the character of beers. This must consequently be taken into account in a classification

intended to serve as a guide to the suitability of natural water supplies for different types of beer. For this purpose waters may first be divided according to their total solids; those containing up to about 10 parts per 100,000 including the best liquors for pale lager beers of Pilsen type. Waters with more than 20 parts per 100,000 of total solids may be regarded as hard. The typical waters of Burton-on-Trent, Dortmund, Dublin and Munich come in this division. They contain comparatively small quantities of salts other than the sulphates and carbonates of calcium and magnesium and, apart from their total solids, are characterised best by their carbonate ratios, $(\text{Ca}^{++} + \text{Mg}^{++}) : \text{CO}_3^{--}$.

In the absence of appreciable quantities of sodium chloride or nitrate, the difference between the two sides of the ratio represents the quantity of sulphate ions present. Thus 100 : 100 means that the water contains calcium and magnesium carbonates only, or that the carbonate, actually bicarbonate ions, are present in quantity equivalent to the sum of the calcium and magnesium ions. 100 : 50 means that the deficit of carbonate ions is made up by sulphate ions and that the water contains equivalent quantities of carbonates and sulphates or weights of CO_3^{--} and SO_4^{--} in the proportion 30 : 48. In many other brewing liquors the error involved in this classification is not great, as the comparatively small quantities of chloride and nitrate present are balanced by sodium.

It follows from the reduction in the hydrogen ion concentration of the mash and wort produced by a liquor containing calcium carbonate or bicarbonate only that the acid-depressing power of one equivalent of CO_3^{--} or HCO_3^{-} is greater than the acidifying power of one equivalent of Ca^{++} . Hence a liquor characterised by a carbonate ratio of 100 : 100 is an acid-reducing liquor. A liquor containing a considerably higher proportion of calcium or less carbonate is required to increase the acidity of the mash over that produced by distilled water. Generally a lower carbonate ratio than 100 : 50 is required. The occurrence of magnesium in varying quantity alters the properties of the liquor to some extent and consequently the ratio $\text{Ca} : \text{Mg}$ could, with advantage, also be given. This refinement is not, however, adopted in the suggested classification. It appears from the analyses given in Tables 135 and 136, that increase in carbonate ratio broadly corresponds with decrease in total solids, and no attempt is made to group the waters according to their total solids, but this must be taken into account when an attempt is made to judge the probable effect of any liquor on beer character.

There must be considerable uncertainty in regard to the effects of the liquor ions on the p_{H} of the mash on account of the complicated nature of the phosphate reactions and presence of other

malt constituents which influence it. Consequently the ratio of the active ions found by analysis can only provide a rough guide to the probable influence of the liquor and its actual effect under specified conditions must be found by trial. The removal of a large and rather indefinite proportion of the calcium and magnesium carbonates by boiling previous to mashing also involves complications, which are not easy to allow for.

The presence of salts of the alkali metals, sodium and potassium, in quantity greater than is balanced by Cl' and NO_3' disturbs the carbonate ratio by displacing Ca'' and Mg'' by Na' and K' and may materially increase the CO_3'' indicated by it. Excessive quantities of sodium and potassium also materially influence the character of the beer produced, as do comparatively large proportions of Cl' or NO_3' . Waters containing these ions, represented by sodium chloride, nitrate, sulphate and carbonate, in quantities greater than those given in the typical analyses of brewing liquors have consequently been separated in groups less suitable for brewing.

TABLE 135.—CLASSIFICATION OF HARD BREWING WATERS
(PARTS PER 100,000)

	Car- bonate ratio	Total solids	Na	Mg	Ca	NO_3	Cl	SO_4	CO_3	Geological formation
GROUP A.										
1. Burton-on-Trent	13	219.2	4.6	8.2	51.2	4.3	6.7	130.1	14.1	Keuper marl
2. Burton-on-Trent	25	122.6	3.0	6.2	26.8	3.1	3.6	65.8	14.1	Gravel beds
3. Burton-on-Trent	39	81.1	4.3	5.8	15.6	5.0	7.3	29.3	13.8	" "
4. Bedfordshire ..	49	78.8	6.0	0.9	19.0	4.8	3.1	30.0	15.0	Lias
GROUP B.										
5. Co. Durham ..	54	76.5	7.4	3.5	14.4	1.2	11.4	21.1	16.5	Magnesian Limestone
6. Dortmund ..	60	101.2	6.9	2.3	26.0	—	10.7	28.3	27.0	Gravel beds
7. Gloucestershire	60	67.8	4.5	4.0	13.6	0.3	3.6	23.5	18.3	Magnesian Limestone
8. Bedfordshire ..	66	55.5	4.6	0.8	13.9	0.6	3.0	17.6	15.0	Oolites
GROUP C.										
9. Lancashire ..	68	61.5	3.9	4.5	12.1	0.3	6.7	14.0	20.0	New Red Sandstone
10. Lincolnshire ..	69	45.8	3.4	0.4	12.2	4.0	3.0	9.6	12.2	Lower Oolite
11. Edinburgh ..	70	80.0	9.2	3.6	14.0	3.1	6.0	23.1	21.0	Old Red Sandstone
12. Yorkshire ..	77	41.2	2.3	1.7	10.5	1.8	3.0	6.6	15.3	New Red Sandstone
13. Lancashire ..	78	24.7	1.6	1.4	5.5	1.7	2.4	2.9	9.2	" "
14. Berkshire ..	80	30.3	0.5	0.9	10.0	0.5	3.6	0.6	14.2	Chalk
GROUP D.										
15. Gloucestershire	85	27.7	0.9	0.6	8.8	1.0	1.6	2.4	12.4	Lias
16. London M.W.B.	85	32.0	2.4	0.4	9.0	0.3	1.8	5.8	12.3	"
17. Nottinghamshire	85	24.6	1.2	3.2	3.6	0.2	1.6	3.4	11.4	New Red Sandstone
18. Surrey ..	86	29.7	1.6	0.2	9.3	2.6	2.3	1.4	12.3	Chalk
19. Hertfordshire ..	92	44.6	3.8	0.7	11.8	3.2	3.5	4.5	17.1	"
GROUP E.										
20. Munich, Dublin	97	27.5	0.1	1.9	8.1	0.3	0.1	0.5	16.5	"
21. Lancashire ..	100	23.9	2.7	1.4	4.4	0.9	1.7	2.7	10.1	New Red Sandstone
22. Lancashire ..	100	38.4	1.9	3.4	8.4	—	1.7	1.8	21.2	" "

CLASSIFICATION OF BREWING LIQUORS § 348

It will be noticed that the hard brewing liquors classified in Tables 135 and 136 in accordance with their carbonate ratios fall in groups around the type liquors given in Chapter XVIII. This ratio is consequently very significant as an indication of the purpose for which the liquor is suitable. A low proportion of CO_3 , in absence of undue quantities of sodium chloride or nitrate, typifies a pale ale liquor, while a carbonate ratio approaching 100 : 100 indicates that the water is suitable for dark mild ales, dark lager or stouts. Other liquors are intermediate in character and their position in the classification suggests the type of beer they would produce and the nature of the treatment they would require for pale ales.

TABLE 136.—HYPOTHETICAL SALTS IN BREWING WATERS
(PARTS PER 100,000)

	Carbonates			Sulphates			Chlorides			Nitrates		
	Ca	Mg	Na	Ca	Mg	Na	Ca	Mg	Na	Ca	Mg	Na
GROUP A.												
1. Burton-on-Trent	23.5	—	—	142.1	37.2	—	—	2.9	7.6	—	—	6.0
2. Burton-on-Trent	23.5	—	—	59.2	30.0	—	—	1.0	4.7	—	—	4.2
3. Burton-on-Trent	23.0	—	—	21.8	17.4	—	—	5.7	6.4	—	—	6.8
4. Bedfordshire	25.0	—	—	30.6	4.7	6.9	—	—	5.1	—	—	6.6
GROUP B.												
5. Co. Durham	27.5	—	—	11.6	16.2	—	—	1.0	17.5	—	—	1.7
6. Dortmund	45.0	—	—	27.2	11.4	—	—	—	17.5	—	—	—
7. Gloucestershire	30.5	—	—	4.8	19.8	6.4	—	—	5.9	—	—	0.4
8. Bedfordshire	25.0	—	—	13.3	3.9	7.5	—	—	4.9	—	—	0.8
GROUP C.												
9. Lancashire	30.4	2.4	—	—	17.5	—	—	1.1	9.7	—	—	0.4
10. Lincolnshire	22.0	—	—	11.6	1.7	—	—	—	5.0	—	—	5.5
11. Edinburgh	35.0	—	—	—	18.0	12.8	—	—	10.0	—	—	4.2
12. Yorkshire	25.5	—	—	1.0	7.3	—	—	0.8	4.0	—	—	2.5
13. Lancashire	13.8	1.3	—	—	3.6	—	—	1.2	2.5	—	—	2.3
14. Berkshire	23.6	—	—	0.9	—	—	0.8	3.5	0.8	—	—	0.7
GROUP D.												
15. Gloucestershire	20.7	—	—	1.8	1.4	—	—	1.1	1.3	—	—	1.4
16. London M.W.B.	20.5	—	—	2.7	1.8	3.6	—	—	2.9	—	—	0.4
17. Nottinghamshire	9.0	8.4	—	—	3.9	0.4	—	—	2.6	—	—	0.3
18. Surrey	20.5	—	—	2.0	—	—	1.6	0.4	1.6	—	—	3.6
19. Hertfordshire	28.5	—	—	1.4	3.4	1.1	—	—	5.8	—	—	4.4
GROUP E.												
20. Munich, Dublin	20.1	6.2	—	—	0.7	—	—	0.2	—	—	—	0.4
21. Lancashire	21.0	11.9	—	—	—	2.6	—	—	2.8	—	—	—
22. Lancashire	11.9	4.9	—	—	—	4.0	—	—	2.8	—	—	1.2

(348) Less Satisfactory Brewing Liquors.

In many cases it is necessary to make use of liquors containing an excess of certain ions which militate against their general

utility and give the beer some special character or make treatment difficult. Many of these would fall in the groups specified in Table 135, were it not for the high proportion of sodium salts or excessive quantities of chlorine. The latter variation does not necessarily alter the carbonate ratio, since chlorine is generally accompanied by sodium. The nitrates stand in a rather different category, since they may, in comparatively small quantity, present a serious objection to waters which would otherwise be classed as excellent brewing liquors. Peaty moorland waters may also, after purification, closely resemble the Pilsen water. A short description of some of the commoner types is given in Table 137.

TABLE 137.—LIQUORS PRESENTING SOME DIFFICULTIES IN BREWING

Saline composition	Uses	Geological formations
G) <i>Sodium sulphate waters.</i> Containing a high proportion of SO_4 with Na predominantly present. Difficulty in treatment in that sodium is not removable. Flavour of beers not so attractive as with calcium salts.	General	Lias
(H) <i>Alkaline waters.</i> Containing mainly sulphate and carbonate of sodium with smaller proportions of Ca and Cl. Cannot be successfully treated for pale ales.	Stout (sweet)	Chalk under London Tertiaries
(I) <i>Nitrate waters.</i> Containing NO_3 in excess of about 5 parts per 100,000, usually with Na. In many cases waters containing between 5 and 10 parts per 100,000 of NO_3 are successfully used for pale and mild ales when Ca : CO_3 ratio is high. In other cases the yeast suffers.	General	Chalk
(J) <i>Salt waters</i> with high proportions of NaCl. Other constituents vary. Detrimental to fermentation if NaCl is in excess of 50 parts per 100,000.	Full mild ales and stouts	Sea coast or near salt deposits, in Trias, etc.
(K) <i>Peaty moorland waters.</i> Very soft, but sometimes brown with organic matter and rather acid. Use depends on purity and ease of treatment.	General	Surface waters, Millstone grit etc.

TABLE 138.—ANALYSES OF WATERS OF LESS SATISFACTORY TYPES
(PARTS PER 100,000)

	Total Solids	Na and K	Mg	Ca	NO_3	Cl	SO_4	CO_3	CO_2 ratio	Geological formation
1. Burton-on-Trent	191.3	23.9	4.8	32.4	—	24.8	92.2	13.2	22	L. Keuper
2. Cheshire ..	46.2	8.1	2.0	6.4	0.6	24.1	1.4	3.6	25	New Red Sandstone
3. Cheshire ..	22.0	1.6	1.6	4.2	0.6	7.5	2.0	4.5	44	" " "
4. Northamptonshire	64.7	18.6	—	3.6	—	9.3	30.2	3.0	55	Lias
5. Bedfordshire	49.7	1.9	0.3	14.7	9.7	3.9	5.0	14.2	62	Chalk
6. Norfolk ..	29.0	1.3	0.3	8.5	4.4	2.8	3.0	8.7	65	Chalk
7. Burton-on-Trent	68.2	10.8	2.6	10.4	—	11.4	16.8	16.2	73	Bunter
8. Lancashire ..	66.8	10.6	3.5	9.4	0.3	7.3	14.1	21.6	94	"
9. Surrey ..	31.1	4.3	2.1	4.9	—	2.7	3.2	13.9	110	Chalk
10. London ..	47.2	9.9	2.0	5.3	0.7	6.1	7.6	15.6	122	Chalk under Tertiaries
11. Northants. ..	64.2	14.5	1.0	8.4	—	6.4	14.4	19.5	130	Lias

Analyses of waters of each of the groups referred to and of others intermediate in composition are included in Tables 138 and 139.

TABLE 139.—HYPOTHETICAL SALTS IN WATERS
(PARTS PER 100,000)

	Carbonates			Sulphates			Chlorides			Nitrates		
	Ca	Mg	Na /K	Ca	Mg	Na /K	Ca	Mg	Na	Ca	Mg	Na /K
1. Burton-on-Trent	22.0	—	—	80.2	24.0	24.1	—	—	40.9	—	—	—
2. Cheshire ..	6.0	—	—	2.0	—	—	9.4	8.1	19.9	—	—	0.9
3. Cheshire ..	7.5	—	—	2.7	—	—	1.1	6.2	3.5	—	—	0.8
4. Northamptonshire	5.0	—	—	5.5	—	38.9	—	—	15.3	—	—	—
5. Bedfordshire ..	23.7	—	—	7.1	—	—	6.1	—	—	3.8	2.1	7.0
6. Norfolk ..	14.5	—	—	4.3	—	—	3.9	0.4	—	1.0	4.9	—
7. Burton-on-Trent	26.0	0.8	—	—	12.0	10.7	—	—	18.7	—	—	—
8. Lancashire ..	23.6	10.4	—	—	2.8	17.6	—	—	12.1	—	—	0.4
9. Surrey ..	12.3	7.3	2.3	—	—	4.7	—	—	4.4	—	—	—
10. London ..	13.2	6.9	4.9	—	—	11.2	—	—	10.0	—	—	0.9
11. Northants. ..	21.0	3.4	8.0	—	—	21.3	—	—	10.5	—	—	—

The carbonate ratio of the deep bore water from Burton-on-Trent, No. 1 in Table 138, is very low but it contains a high proportion of sodium chloride and more sodium sulphate than is shown in the water given as typical of pale ale liquors. It would tend to give fuller mild ales but a harshness with highly hopped beers. The Bunter water from the same town, No. 7, resembles No. 1 in the high proportion of sodium salts, actually a greater percentage of the total solids than in the much harder Lower Keuper water.

No. 8 is also from the Bunter formation, but from a place some 70 miles from Burton. The two waters have very much in common, differing mainly in the higher proportion of carbonate and correspondingly reduced sulphate and chloride in the Lancashire water, giving the latter a higher carbonate ratio. A similar correspondence exists between the waters Nos. 1 and 9 in Tables 135 and 136. The chief difference in these is in their gypsum content. This makes a material difference in their brewing properties, but the Lancashire water is a very good brewing liquor and could very readily be built up by addition of gypsum and a smaller quantity of magnesium sulphate to resemble the Burton water as nearly as thought desirable.

(349) Saline Waters.

The two waters from Cheshire, Nos. 2 and 3 in Table 138, differ mainly in the quantities of chlorides they contain and it may be noted that the chlorine has to be distributed between calcium,

magnesium and sodium in an attempt to represent the saline constituents. Waters of this type produce full mild ales, the flavour depending on the quantity of chlorides present.

(350) Nitrate-containing Waters.

Nos. 5 and 6 contain rather high proportions of nitrates, typical of many waters from the chalk in various parts of the country. Little difficulty is to be anticipated from liquors with analyses corresponding to No. 6. They would probably prove satisfactory for running beers and could readily be treated for pale ales. No. 5, however, contains definitely too much nitrates. Liquors of this type may lead to yeast degeneration and necessitate frequent changes of pitching yeast.

(351) Sodium Sulphate Waters.

No. 4 contains a very high proportion of sodium sulphate, which is difficult to deal with except by addition of calcium ions in the form of calcium chloride, a treatment which, in this case, would unduly raise the chlorine content. The benefit of such treatment for pale ales would be problematical and could only be judged by results, since there is no theoretical guidance to be relied on. In such waters as this the carbonate ratio is already low and would not be greatly reduced by boiling, but probably a small addition of calcium ions would be advantageous to complete the phosphate reactions in the mash tun in a way that appears desirable for pale ales.

(352) Alkaline Waters.

This group is represented by Nos. 9, 10 and 11, all from the London area. In these the excess of CO_2 is balanced by sodium and with the sodium carbonate there usually occur both sodium sulphate and chloride in considerable quantities. Formerly liquors of this type were considered suitable for the production of sweet stouts and they can no doubt be used for this purpose with success, but they are now regarded as most objectionable brewing liquors on account of their high alkalinity. They are not suitable for pale ales but a method of treatment with lime and acid for mild ales is given in Section 369.

(353) Summary.

The influence of the liquor on the character of beer brewed with it is attributed to the quantity and nature of the dissolved salts or their ions and the reactions between them and various constituents of the malt and hops. Reactions of calcium and magnesium

with phosphates derived from the malt lead to an increase in the acidity of the mash which has an activating influence on starch-converting, proteolytic and other enzymes. Reactions between the bicarbonate or carbonate ions and the phosphates reduce the acidity of the mash and restrict the activity of the enzymes. The increase of acidity has other beneficial effects on the coagulation of proteins during boiling, on the brilliance of the beer and on the hop flavour, while reduction of acidity has harmful effects on the colloidal state of various constituents of the beer and on the hop flavour. Calcium ions, whether derived from gypsum, calcium bicarbonate or calcium chloride, are consequently beneficial in their effects, while the carbonates are generally detrimental if present in more than small quantity. Magnesium operates in a similar manner to calcium, with certain differences attributable to the greater solubility of its carbonate and phosphates. Chlorides affect hop flavour and nitrates are harmful to yeast.

The quantity of salts found desirable for different types of beer varies greatly. A very hard water with a high proportion of gypsum is generally preferred for pale ales. A very soft water is desirable for pale lagers. Moderately hard liquors containing carbonates almost exclusively are best for full mild ales, dark lagers and stouts. The sodium salts are undesirable if present in comparatively large proportions. The sulphate is detrimental to flavour, the chloride in moderate quantity gives fulness but a harsh flavour with strongly hopped beer, the carbonate is very harmful on account of its effect in reducing the acidity of the mash.

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CHAPTER XX

LIQUOR TREATMENT

WATER SOFTENING AND DECARBONATION

(354) Water Purification and Treatment.

It is rarely that any sort of purification, other than filtration of suspended particles or removal of small quantities of iron or of free CO_2 , which causes damage to iron pipes and tanks, is required with brewery water supplies. The iron and CO_2 are generally removed during softening or other treatment but can be dealt with by aeration. By liquor treatment is understood the addition of such salts as are lacking in the raw supply or removal of others that occur in excessive quantity, with the object of adjusting the composition of the liquor to that most suitable for the type of beer brewed. It usually means imitation of the best natural brewing waters, so that the additions are never more than small in quantity. The partial removal of calcium and magnesium carbonates is generally an essential part of liquor treatments and in many cases the only treatment required. Boiling is expensive and generally unnecessary for sterilisation with the pure supplies almost everywhere available, but it is the most satisfactory process for the hard gypseous waters, such as those of Burton-on-Trent. The less costly process of precipitation with lime has been almost universally adopted in lager breweries, where the object is to obtain a very soft liquor for beers of Pilsener type. The removal of carbonates is referred to as decarbonation.

(355) Decarbonation by Boiling.

The ions in solution in a carbonate water are HCO_3' and Ca'' or Mg'' . The bicarbonate ions are converted into CO_3'' and undissociated H_2O and CO_2 by boiling, but removal of the carbonates by precipitation in this way, according to the equation :



is never complete on account of the slight solubility of CaCO_3 and the much greater solubility of MgCO_3 . Their solubilities vary with the temperature but that of calcium carbonate may be

taken as about 2.2 parts per 100,000 at ordinary temperatures, while magnesium carbonate is soluble in cold water to the extent of about 10 parts per 100,000, but is rather less soluble at higher temperatures, so that boiling under pressure is more effective in precipitating it. The calcium carbonate content of water is rarely reduced below 4 or 5 parts per 100,000 and may remain at 10 or 20 parts per 100,000 after boiling for half an hour under atmospheric pressure, while the magnesium carbonate content may show very little reduction. The relative proportions of calcium, magnesium and sodium present materially affect the equilibrium reached. Increase of the calcium ratio by addition of calcium chloride or sulphate increases the precipitation of calcium carbonate in presence of magnesium and sodium, but very variable results are obtained with different waters. The solubility of magnesium carbonate makes it necessary to convert it into the almost insoluble hydroxide by chemical means, when as complete removal as possible is required for boiler or other purposes.

The carbonates of both calcium and magnesium are much more completely removed by boiling under pressure with constant agitation. A very efficient and economical decarbonation is secured by use of special plant described by Siau,¹ in which it is possible, by adoption of the principle of recuperative heating, to reduce the quantity of calcium carbonate from between 14 and 19 parts per 100,000 to 2.5 without sensibly greater steam consumption than is necessary to raise the temperature of the water to 150° Fahr. for mashing. The plant for dealing with 100 barrels of water per hour consists of 5 boiling tanks heated by steam coils and operated under a pressure of 5 lb. The raw water is pumped through a heat exchanger of the Paraflo type, in the first section of which it is heated by outflowing boiling water, in the second by steam given off from the boiling elements and in the third part or superheater, its temperature is raised to about 220° Fahr. The boiling decarbonated liquor flows from the tanks by gravity through the heat exchanger, where it is cooled to 150° Fahr. for mashing and heats the incoming raw water from 50° to 110° Fahr. Any additions of calcium sulphate or chloride required to complete the liquor treatment are made before boiling, in order to reduce the solubility of calcium carbonate and assist in the removal of magnesium and sodium bicarbonates. The boiling time is reduced to about 15 minutes under a pressure of 5 lb.

Fig. 60 illustrates an automatic arrangement on the Richter system. In this the carbonates are precipitated by agitation with steam at a comparatively high pressure in a closed vessel, which may be 22 feet long by 3 ft. 6 in. diameter for an output of about 2,000 gallons an hour. Steam is admitted to this decar-

bonating drum at a pressure of 60 lb. per square inch through an eccentrically arranged inlet tube fitted with special nozzles. The water is kept in a state of turbulence at between 260° and 300° Fahr. by means of baffle plates. The heated water is passed, after filtration in a closed vessel, through a counter-current heat exchanger where it is cooled to mashing temperature and heats the incoming raw water. The pressure filter is of the normal closed sand and gravel type and is cleansed periodically with cold water and compressed air. The precipitated carbonates are delivered from it to a sludge drum.

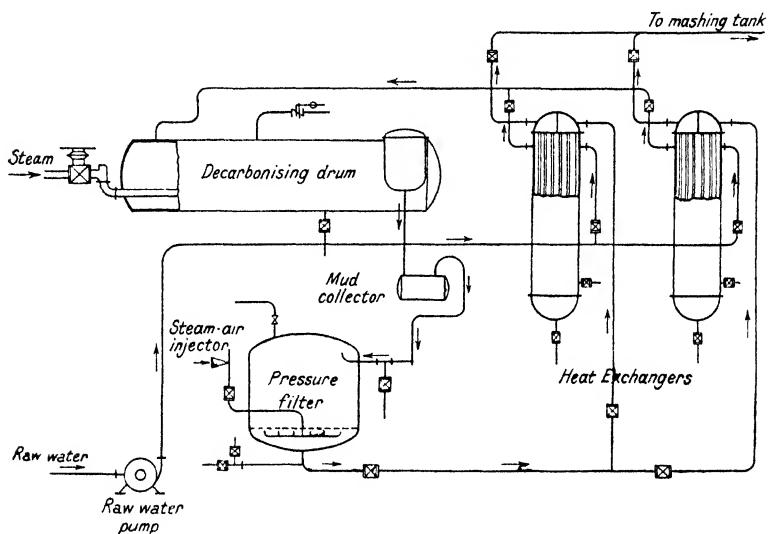


FIG. 60

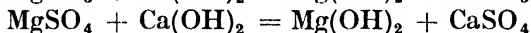
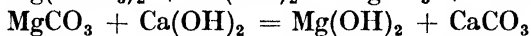
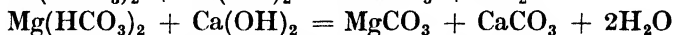
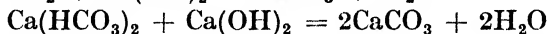
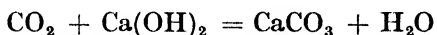
AUTOMATIC DECARBONATING PLANT

(356) Decarbonation by Addition of Lime.

Removal of calcium carbonate by addition of lime at ordinary temperatures is satisfactory with waters which contain only a small proportion of magnesium salts. It is cheaper than boiling but the space required is great, particularly if a number of large tanks are necessary to maintain a continuous supply of softened liquor. The lime water reagent should be made by vigorously stirring excess of pure quick lime, free from iron and silica, in water until as much as possible is dissolved. The undissolved lime is allowed to settle and only clear lime water drawn off for use. This may be mixed with the bulk of raw water by means of compressed air. After at least 10 hours and preferably 48 hours, during which 80% of the precipitated carbonate settles, the liquor is passed through sand filters, where the reaction is speeded up greatly

should it not have been completed in the tanks, to the liquor tanks with its hardness reduced to 4° Clark (grains per gallon CaCO_3).

The chief reactions involved when the calculated quantity of a saturated solution of pure lime is added are :



In practice the reactions are never complete, the equilibrium varying according to the presence of free CO_2 , the solubility of CaCO_3 and MgCO_3 and the ratio of calcium, magnesium and sodium ions, while the maximum precipitation requires some 2 or 3 hours. It is also difficult to avoid a slight excess or deficit of lime, but the hardness can be reduced to between 5° and 3° Clark. An increase in the calcium ratio by addition of calcium chloride leads to a more complete precipitation of calcium carbonate, as in the boiling process. If sand filters are not employed there is risk of carrying some of the precipitate to the mash tun, where it acts adversely to the desired reduction of p_{H} . Precipitated calcium carbonate settles in about 3 hours in a tank, but particles to the extent of about 1 grain per gallon remain suspended and care should be taken to prevent any larger quantity finding its way to the mash tun.

The solubility of CaO in water is about 1.36 grams per litre or 95 grains per gallon, but usually only between 80 and 90 grains per gallon will dissolve. The quantity of CaO in solution can be found by titrating 50 ml. with $\text{N}/10$ HCl , using phenol-phthalein as indicator. 50 ml. of the water to be softened is titrated in a similar way with methyl orange as indicator. The quantity of CaO in grams per litre or grains per gallon in the lime water or in the water to be treated is found by multiplying the number of ml. of decinormal acid required by 0.056 or 0.392 respectively. For each grain or gram found in a gallon or hectolitre of the water, it is necessary to add one grain or one gram to that volume of the water. From this and the known strength of the lime water, the volume of the latter in gallons or litres can be calculated. Thus if the lime water was found to contain 80 grains per gallon of CaO and the water to be treated 16 grains per gallon,

16 ÷ 80 or $\frac{1}{5}$ gallon of lime water would be required for each gallon of water to be treated.

Since an excess of lime water is harmful, it is essential to test the softened water by addition of a few drops of phenol-phthalein to

a small sample. No red colour should be produced. If excess is found, more of the untreated water must be added.

On account of the inefficiency of this process, particularly in presence of magnesium bicarbonate, many brewers of pale lager beer find it advisable to compensate for the excess of bicarbonate left in the water after softening by adding an equivalent quantity of gypsum.

Intermittent systems of the type described are accurate when carefully controlled, but automatic plants requiring much less tank capacity are available. In these, continuous additions of accurately measured quantities of lime water are made by mechanical means and the treated liquor filtered. By the introduction of waste steam such plants can be used for hot softening with increased efficiency. The reaction may be hastened and made more complete by the catalytic action of suitable contact masses. For this purpose some of the precipitate from a previous softening may be mixed with subsequent softenings, in which it will act as the necessary nucleus for precipitation. By combination of thorough mixing and use of a catalyst, the time of reaction can be reduced from 2 or 3 hours to between 7 and 10 minutes, while the quantity of magnesium removed will be increased.

Removal of magnesium by conversion to magnesium hydroxide requires a considerable excess of lime and increase of the p_H of the treated liquor to 10.5 or 11, which would not be suitable for brewing. Two methods are available for overcoming this difficulty. In one excess of lime water may be added to the whole of the water, followed by neutralisation with CO_2 or lactic acid, but this has the disadvantage that great care is required to avoid acidification or excess of CO_2 , which is corrosive to iron. The other method introduced in America is known as the "split process." In this, sufficient saturated lime water is added to remove the magnesium as hydroxide or basic carbonate in part only of the liquor. The strongly alkaline treated water is then added to the remainder of the raw liquor to precipitate the bicarbonate of calcium. This process obviously does not remove all the magnesium, since most of the latter present in the second portion of the raw liquor would remain in solution but if, for example, $\frac{5}{8}$ of the water were first treated and then added to the remaining $\frac{3}{8}$, 62.5% of the magnesium would be removed.

(357) Base Exchange System of Softening.

This system is used in some breweries for the removal of small quantities of calcium and magnesium but it is only suitable for waters of low or very moderate hardness or for removal of small quantities of calcium and magnesium after a preliminary softening



Fig. 61
ZEOLITE WATER-SOFTENER PLANT (J. W. GREEN, LTD., LUTON)

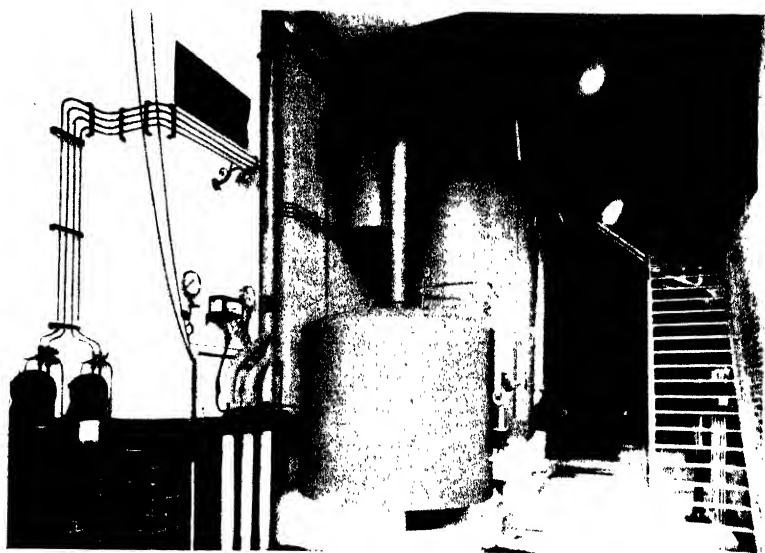
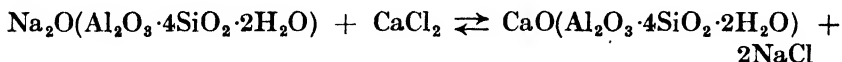


Fig. 62
AUTOMATIC SOFTENING PLANT IN BOILER HOUSE (BRAUEREI HALDENGUT, WINTERTHUR)

Facing page 469]

with lime. This double treatment has the advantage that risk of alkalinity from excess of lime is avoided but at the expense of adding two molecules of sodium salt for each molecule of alkaline earth salt removed, for which reason it is unsuitable for use with hard waters. The following equation shows that all lime and magnesium salts and not only the carbonates are removed by a process of "base exchange."



The sodium aluminium silicate shown in this equation is representative of the natural or artificial zeolites or permutit used as softening agents. The operation is simple and efficient, consisting in passing the water through the zeolite, as through a filter, when the base exchange takes place. After the whole of the sodium has been replaced by calcium or magnesium, the zeolite is regenerated by passing a solution of common salt in the opposite direction. The process finds a special application in bottling stores to remove the lime salts which otherwise contribute to the bloom on bottles washed in caustic soda, the presence of the sodium salts produced causing no difficulty in this case.

A small plant erected in a bottling store is shown in Fig. 61. This consists of two cement-lined mild steel tanks, 4 ft. 9 inches in diameter, containing the zeolite and used alternately for softening and regeneration. These are connected with the necessary pipe lines and valves to the water supply and outlet and to the mild steel brine tank. Each tank will operate at a rate of 3,000 gallons an hour and soften 13,400 gallons of water, with a hardness of 21° Clark, to zero hardness before regeneration is necessary. The latter process requires 8.5 lb. of salt per 1,000 gallons softened. A hardness testing apparatus is attached to each tank.

(358) Electro-Osmose.

It is possible completely to remove the dissolved salts from water by taking advantage of their ionic dissociation and of the migration of the ions to the anode and cathode when an electric current is passed. This process, known as electro-osmose, would seem to offer many possible advantages when complete or partial softening is required, irrespective of the nature of the salts removed but without the power selectively to remove undesirable salts. So far it has not, however, been brought much beyond the large scale experimental stage. The necessary plant consists of rectangular vessels divided into three compartments by two transverse diaphragms, through which the ions but not the water can pass. Raw water is placed in the inner compartment, with the

positive and negative electrodes in the two others. As the current is passed the cations and anions migrate through the diaphragms to the cathode and anode respectively, across which a current of water is continually flowing. A number of elements are connected in a continuously working plant arranged for the flow of water from one to another.

(359) Softening of Boiler Feed Waters.

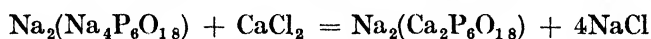
The formation of scale in the boiler plant is very troublesome with gypseous water supplies. The nature of the deposit formed in boilers, economisers, tubes, etc., depends largely on the effect of rising temperature on the solubility of the salts concerned. When this increases with rising temperature, as in the case of calcium carbonate, the salt deposits as a mud on the hotter parts of the boiler and as a hard scale on the cooler. When it decreases with rising temperature, as in the cases of calcium sulphate and silicate, a hard scale forms on the heated surfaces. Hence the hard scale on boiler tubes is largely calcium sulphate or silicate. The salts are most satisfactorily removed in external softening plants, usually by addition of soda ash and lime. The quantity of sodium carbonate used is that required to convert the calcium and magnesium sulphates, chlorides and nitrates present into carbonates and the efficiency of the lime-soda process in presence of magnesium salts is greatly increased by adding to the reagent mixture 1 or 2% of sodium aluminate which coagulates the magnesium precipitate.

Very efficient external, automatically-controlled softening plants are available. That shown in Fig. 62 operates continuously on the Neckar system and consists of five tanks, a reagent tank with soda-dissolving and lime-slaking vessel above, a mixing tank for water and reagent, a reaction tank in which the softening is completed at a moderately high temperature, an expansion cylinder above and a gravel filter from which the softened liquor flows to a closed vessel from which a feed pump delivers it to the boiler.

Phosphates are now widely used for water softening and have several advantages over the mixture of lime and soda-ash. Thus tri-sodic phosphate can be used in the feed water with greater safety and has other advantages in that the calcium and magnesium phosphates are less soluble than the corresponding carbonates, its action is more rapid and it also serves as a disincrustant. Phosphates should not, however, be added to the boiler unless the water has been reduced to 4 or 5 degrees Clark in an external softener. They remove scale already formed by converting the calcium carbonate, sulphate or silicate into phosphate and the corresponding sodium salt. For this purpose the boiler is left

under pressure for some days and fed with water containing 0·2% of trisodic phosphate, samples being taken from time to time to see that the concentration does not fall below 0·1%, which is that usually employed during service.

Sodium hexametaphosphate, $(\text{NaPO}_3)_6$, obtained commercially as Calgon in which it is mixed with a small proportion of sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, is another useful softening reagent. It has the curious property of forming complex soluble compounds with calcium salts, which are thus not precipitated in economisers, and it removes boiler scale by forming these salts. The following equation represents the formation of one of these soluble salts by addition of excess of hexametaphosphate to calcium chloride solution. The solution will not give the reactions of calcium.



If the clear treated water is used in the boiler, reactions occur at 212° and above, which cause precipitation of calcium and magnesium phosphates.

TREATMENT OF BREWING LIQUOR

(360) Empirical Methods of Treatment.

It may be accepted that the natural waters used for brewing at Burton-on-Trent, Dublin, Pilsen, Munich and other well-known brewing centres have the most suitable composition for beers of the type with which each is associated. This led to the view that it was necessary to treat other waters by addition of missing constituents or removal of excess of others, so that the analyses should approach as closely as possible to that of a water known to be suitable for the kind of beer required. Empirical methods of treatment of this kind are still the most commonly adopted and, in England, follow almost literally the lines laid down by Southby in the last half of the nineteenth century. He held that liquors for pale ale should resemble those of Burton-on-Trent as closely as possible and have the following characteristics.

(1) The sulphuric acid present should be just sufficient to combine with the lime and magnesia not precipitated as carbonates on boiling.

(2) The sulphates should be present in the proportion of 3 of calcium sulphate to 1 of magnesium sulphate.

(3) The most suitable limits for brewing beers with the true Burton characteristics were :

CaCO_3 and MgCO_3	10–20	grains per gallon
SO_3	15–40	„ „
Cl	2–3½	„ „

The great difference between the Burton and Dublin waters, of which the latter was taken as the type for stouts, consisted in the almost complete absence of sulphates from the Dublin water and the small amount of chlorides in it. Further, when boiled, it had a distinct alkaline reaction due to about 1·2 grain per gallon of magnesium carbonate with a little alkaline silicates.

Southby concluded that carbonates of the alkaline earths were essential constituents of brewing liquors, since a proportion found their way into the mash tun, even after the water had been boiled for an hour. 10 grains per gallon were held to be sufficient and any less than 4 to 5 grains not enough. This is the limit to which the carbonates are generally reduced on boiling.

Chlorine was held to be "an essential constituent for fulness in ales but not in stouts of Dublin type. Alkaline chlorides should about equal in quantity the alkaline earth chlorides. Sodium chloride was not in itself sufficient to produce the effects, calcium chloride or magnesium chloride should also be added. Addition of calcium chloride also ensured decomposition of injurious sulphates and carbonates of the alkalis. Sulphates of calcium and magnesium were essential for pale ale brewers, the best relative proportions were 1 part of MgSO_4 to 3 parts CaSO_4 ."

(361) Liquors for Top Fermentation Beers.

Southby's conclusions have been accepted with little change down to the present time and provide the basis for liquor treatment in a large number of ale breweries, though many brewers regard the presence of calcium and magnesium carbonates, even in small quantity, as harmful instead of essential for light gravity ales, but they usually insist on the addition of magnesium sulphate for yeast nutrition. There is thus a consensus of opinion among ale brewers that some such liquor composition as is indicated in Table 140 is

TABLE 140.—SALT REQUIREMENTS IN BREWING LIQUORS
FOR ALES AND STOUT
(PARTS PER 100,000. MILLIVALS IN BRACKETS)

	Pale ales 1055—1045	Pale ales 1045—1035	Mild ales 1050—1035	Stouts 1055—1040
Calcium sulphate ..	54·4 (8)—34·0 (5)	34·0 (5)—20·4 (3)	20·4 (3)—6·8 (1)	—
Magnesium sulphate ..	12 (2)— 6·0 (1)	9 (1·5)—6 (1)	6 (1)	6 (1)
Sodium chloride ..	5·9 (1)— 2·9 (0·5)	2·9 (0·5)	11·7 (2)—5·9 (1)	17·5 (3)—11·7 (2)
Calcium chloride ..	5·5 (1)— 2·8 (0·5)	2·8 (0·5)	11·1 (2)—5·6 (1)	16·6 (3)—11·1 (2)

(Grains per gallon = parts per 100,000 \times 0·7)

desirable for beers of the types named and that treatment of liquor should be directed to make up for any deficiencies. The actual figures given in the Table in parts per 100,000 are calculated to give a round number of millival of each constituent when this is added to distilled water, since such figures make treatment calculations more simple. The figures in brackets represent millival, from which the corresponding weights of the individual ions can be calculated by multiplying by their respective equivalent weights. If it is customary to work in grains per gallon, the corresponding figures can be obtained by multiplying those given in parts per 100,000 by 0.7.

It will be observed that the quantities of the several mineral constituents increase with increasing gravity, which is in accordance with the view that they must bear some relation to the phosphates of malt with which they react in the mash tun. Gypsum is added to increase the acidity of the mash and to improve brilliance and delicacy of hop flavour. The chlorides are used to produce fulness of flavour but in reduced quantity in bitter beers, in order that the hop flavour should not be too pronounced. It is probably advisable that the chlorides should consist of the sodium and calcium salts in equal quantity, as suggested by Southby, but common salt is frequently used alone. It is understood that the carbonates are reduced to about 6 or 8 parts per 100,000 by boiling and this is the only treatment indicated with a moderately hard carbonate liquor for stout of Dublin type.

Various methods are adopted to secure analytical figures in the treated liquor corresponding with those given in the Table or such modifications of them as individual experience dictates. These generally depend simply on removal of a large part of the carbonates and the necessary additions to make up for deficiencies in the other salts of the raw liquor. The salts are added to the hot liquor tank, preferably in the form of strong solutions or as a cream with water. The liquor is then well boiled for half an hour or an hour if carbonates are to be removed, and the precipitate allowed to settle before the clear liquor is drawn off for use. The old device of running the water over gypsum blocks is not to be advised, as the quantity dissolved is very difficult to regulate.

The figures in Table 141 may be used as a guide to the quantities of salts required to compensate for deficiencies revealed by analysis of the original water. 1 oz. of an anhydrous salt added to a barrel of liquor yields 12 grains per gallon (more accurately 12.15 grains) of the salt. If calculations are made on this basis, allowance must be made for water of crystallisation in the commercial products. Thus 1 oz. per barrel of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), unless obtained in the anhydrous powdered form, is equivalent to about 10 grains

per gallon of calcium sulphate. 1 oz. per barrel of Epsom salts ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) or 1 fl. oz. per barrel of calcium chloride represent approximately 6 grains per gallon of magnesium sulphate or of calcium chloride.

TABLE 141.—SALT ADDITIONS FOR LIQUOR TREATMENT

Commercial Product	Rate added	Salt or ion added	Resulting additions		
			Grains per gal.	Pts. per 100,000	Millicals N/1000
Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1 oz. per barrel 4 lb. per 100 brls. 3.1 " " "	CaSO_4	9.6 6.2 4.8	13.7 8.8 6.8	2.0 1.3 1.0
Magnesium sulphate .. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	1 oz. per barrel 4 lb. per 100 brls. 4.4 " " "	MgSO_4	5.9 3.8 4.2	8.4 5.4 6.0	1.4 0.9 1.0
Common salt NaCl	1 oz. per barrel 4 lb. per 100 brls. 2.1 " " "	NaCl	12.1 7.8 4.1	17.3 11.1 5.8	3.0 1.9 1.0
Calcium chloride solution 1350–1360 sp. gr.	1 fl. oz. per brl. 4 pints per 100 brls. 3.2 " " "	CaCl_2	6.0 4.9 3.9	8.6 7.0 5.5	1.5 1.3 1.0
Acid potassium sulphate 30% free H_2SO_4	1 oz. per barrel 4 lb. per 100 brls. 2.5 " " "	$\text{SO}_4^{''}$	8.5 5.5 3.4	12.2 7.8 4.8	2.5 1.6 1.0
Sulphuric acid 95% 1.8 sp. gr.	1 fl. oz. per brl. 4 lb. per 100 brls. 1.9 " " "	$\text{SO}_4^{''}$	21.3 7.2 3.4	30.6 10.3 4.8	6.4 2.1 1.0
Lime, anhydrous CaO	1 oz. per barrel 4 lb. per 100 brls. 1 lb. " " "	Ca	12.1 7.8 1.9	17.3 11.1 2.8	6.2 4.0 1.0
Lime, hydrated Ca(OH)_2 , 92%	1 oz. per barrel 4 lb. per 100 brls. 1.5 " " "	Ca(OH)_2	11.2 7.2 2.6	16.0 10.2 3.7	4.3 2.8 1.0

Kainite is a natural mineral obtained near Stassfurt in Prussia and at Kalusz in Galicia. Its composition is very varied, as the three analyses show :

	Per cent.	Per cent.	Per cent.
Potassium sulphate	20	21	33
Magnesium sulphate	—	15	1
Sodium chloride	53	35	40
Potassium chloride	24	2	—
Magnesium chloride	—	12	20
Calcium sulphate	—	2	1
Silica, alumina, etc.	3	1	1
Water	—	12	4
	<u>100</u>	<u>100</u>	<u>100</u>

The quantities of the various constituents of Kainite added in liquor treatment may be calculated from the figures given in Table 141 for common salt by multiplying these figures by the

percentage of the constituent found by analysis and dividing by 100.

When Kainite has been unobtainable, brewers who were accustomed to use it have substituted mixtures of common salt and gypsum.

Calcium chloride is so deliquescent that it is bought in almost saturated solution containing rather less than 10 oz. of calcium chloride in a pint of the solution.

A satisfactory commercial sample of potassium hydrogen sulphate or potassium bisulphate contains about 90% of KHSO_4 and 10% of K_2SO_4 .

(362) Empirical Treatment of an Alkaline Liquor.

Treatment for pale and mild ales of the London deep bore water, shown in Table 124, Section 330, is given as an instructive but rather complicated example of this method of correction. The necessary additions are most readily calculated from the millival of ions given in the first column of the analysis.

Millivals			Millivals		
Sodium	..	4.3	Chloride	..	1.7
Magnesium	..	1.6	Sulphate	..	1.6
Calcium	..	2.6	Carbonate	..	5.2
<hr/>			<hr/>		
8.5			8.5		
<hr/>			<hr/>		

In the first place calcium ions would be added (as calcium chloride solution) in quantity equivalent to the CO_3 not satisfied by Ca and Mg ions. This is $5.2 - (2.6 + 1.6) = 1.0$ millival.

Then sufficient calcium is added to satisfy the SO_4 ions, viz. 1.6 millival in the form of CaCl_2 .

The total quantity of calcium chloride required is thus represented by $1.0 + 1.6 = 2.6$ millivals. This is multiplied by 55.5, the equivalent weight of CaCl_2 and by 0.07 to convert to grains per gallon, giving $2.6 \times 55.5 \times 0.07 = 10.1$ grains per gallon CaCl_2 . According to Table 141 this means 8.3 pints of the saturated solution of calcium chloride per 100 barrels.

The composition of the treated liquor is then found by adding 2.6 millivals to the calcium and 2.6 millivals to the chloride, giving :

Millivals			Millivals		
Sodium	..	4.3	Chloride	..	4.3
Magnesium	..	1.6	Sulphate	..	1.6
Calcium	..	5.2	Carbonate	..	5.2
<hr/>			<hr/>		
11.1			11.1		
<hr/>			<hr/>		

and can be expressed in terms of the hypothetical salts by multiplying each combination assumed to be present by its equivalent weight.

Sodium chloride	..	$4.3 \times 58.5 \times 0.07 = 17.6$	grains per gallon
Magnesium sulphate	..	$1.6 \times 60 \times 0.07 = 6.7$	„ „
Calcium carbonate	..	$5.2 \times 50 \times 0.07 = 18.2$	„ „
		<hr/>	
		42.5	

A considerable proportion of the CO_2 would be precipitated as calcium carbonate and the water would then apparently present a simple case for treatment by addition of gypsum for pale ales. It is, however, a very big assumption to presume that the reactions would actually proceed in the manner indicated. In practice this method of treatment is never quite satisfactory with alkaline waters and in many cases so much calcium chloride would be required to satisfy the sulphate and carbonate originally present that the equivalent quantity of sodium chloride formed would present a difficulty with pale ales. Treatment by addition of sulphuric acid or by the lime-acid process described later would be preferable for waters of this type.

Typical additions to complete the treatment for different kinds of beer would be as follows :

FOR 100 BARRELS

For pale ales :	Calcium chloride	8.3 pints.
	Gypsum	24 lb., giving 37 grains per gallon.
	Kainite	12 lb.
For mild ales :	Calcium chloride	8.3 pints.
	Gypsum	12 lb., giving 18.5 grains per gallon.
	Kainite	18 lb.
For stouts :	Kainite	24 lb.

Many brewers would consider these additions too heavy for light gravity beers and would reduce the gypsum and kainite by half. An alternative treatment to avoid the excess of chlorine could be carried out by adding gypsum in quantity equivalent to the difference between the carbonate and alkaline earth ions, that is,

$$1.0 \times 68 \times 0.07 = 4.76 \text{ grains per gallon}$$

68 being the equivalent weight of calcium sulphate. Calcium chloride would then only be added in sufficient quantity to satisfy the sodium presumed to be combined with SO_4 , that is 1.6 millival or

$$1.6 \times 55.5 \times 0.07 = 6.216 \text{ grains per gallon.}$$

The final analysis in this case would be :

	Millivals		Millivals
Sodium	4.3	Chloride	3.3
Magnesium	1.6	Sulphate	2.6
Calcium	5.2	Carbonate	5.2
	<hr/>		<hr/>
	11.1		11.1
	<hr/>		<hr/>

Calculated to salts this would give :

	Millivals	Grains per gallon
Sodium chloride	3.3	13.51
Sodium sulphate	1.0	4.97
Magnesium sulphate	1.6	6.72
Calcium carbonate	5.2	18.20
	<hr/>	<hr/>
	11.1	43.40
	<hr/>	<hr/>

A considerable proportion of the calcium carbonate would be removed when the liquor was boiled.

(363) Liquors for Lager Beers.

Empirical considerations similar to those which have governed liquor treatment in ale breweries lead to the conclusion that a very soft water of the type used in Pilsen should be the most satisfactory for pale lager beers of delicate but pronounced bitter flavour, while a carbonate water similar to that of Munich is best adapted to the production of full-flavoured dark beers. The fame of the Dortmund beers suggests that a moderately hard gypseous liquor is suitable for pale lagers of the type characteristic of that city. These considerations have great weight in the liquor treatment at Continental breweries, but in America a liquor hardened very much in accordance with British tradition is in very general favour for the beers brewed with a high proportion of maize or rice grits. The addition of gypsum, magnesium sulphate and chlorides in appropriate proportions is commonly referred to in America as Burtonizing.

Since carbonate waters of moderate hardness are the most commonly available, it is usual to soften or decarbonate them by one of the methods already described. Of these the lime treatment is most widely adopted. It is not permissible completely to soften the liquor, at the risk of making it alkaline. It is also found that a very soft liquor tends to give a soft beer, devoid of flavour, unless the hop rate is on the high side. A moderate quantity of carbonates tends to make the flavour fuller and

stronger. In general the calcium carbonate should not be reduced below about 5 parts per 100,000.

The characteristics of the malt have a considerable bearing on the treatment in any particular case. If it is fully modified and contains more than the usual acidity, a harder liquor can be used with safety and in some cases an addition of gypsum or KHSO_4 in quantity equivalent to the carbonate left after softening gives good results. Many brewers reduce the carbonate hardness to about 5 or 6 German degrees, or about 10 parts per 100,000 of calcium carbonate, and add rather more than the same amount of gypsum.

The quantity of gypsum required for equivalence with the carbonates present in the water after decarbonation can be found by titrating 100 ml. with decinormal acid in presence of methyl orange. Each ml. of decinormal acid required to neutralise the water means that it contains 5 parts per 100,000 of CaCO_3 and that sufficient gypsum should be added to bring the CaSO_4 content of the liquor up to 6.8 parts per 100,000. According to Table 141, 3.1 lb. of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or 2.45 lb. of anhydrous gypsum would be required for each ml. of acid required for neutralisation, presuming that the water did not already contain gypsum. In some cases this quantity can be doubled with advantage.

The results of some large scale brewing experiments by Lüers,² may be quoted as examples of the differences in beer character produced by various methods of liquor treatment. Their effects on the composition of the liquor are given in Table 142.

TABLE 142.—TREATMENT OF LIQUOR FOR PALE LAGER IN EXPERIMENTAL BREWS

Brew	Liquor used	Hardness, CaO parts per 100,000		
		Total	Temporary	Permanent
1	Untreated	15.0	14.2	0.8
2	Lactic acid added to reduce p_H of wort by 0.26	—	—	—
3	Softened by lime	4.0	3.2	0.8
4	As 3 with added gypsum ..	10.2	3.2	7.0
5	Neutralised with lactic acid ..	15.4	—	15.4

Softening and neutralisation lead to an increase in the nitrogen content of the finished worts and this was particularly marked in 5 and 3. Addition of lactic acid previous to boiling with hops reduced the nitrogen content of the wort by increasing the coagulation of proteins. Formol titration showed that Brew No. 5 contained the greatest quantity of the most fully degraded nitrogen

compounds. The increase in the proportion relative to total nitrogen in No. 2 was due to reduction of the total nitrogen by coagulation in the copper. The assimilation of nitrogen by the yeast was also greatest in No. 5, but was low in 2. Softening by any method led to an increased amount of phosphoric acid in the wort, but there was little difference in the ratio between inorganic and organically combined phosphorus. This ratio was about 5 : 1 in the worts and $4\frac{1}{2}$: 1 in the beers. Analyses of the worts and beers are given in Table 143.

TABLE 143.—ANALYSES OF WORTS AND BEERS FROM DIFFERENTLY TREATED LIQUORS

Brew	Extract	p_H	Acid. ml. N/10 in 100 ml.		N. mgm. in 100 ml.		Formol N as % total	Phos- pho- tung- stic N	P_2O_5	Maltose % of solids	Colour
			1	2	Total	Formol					
WORTS											
1	10.22	5.94	6.75	17.52	80.08	29.75	27.15	17.08	67.70	55.6	0.75
2	10.48	5.64	6.50	16.50	76.72	29.75	38.78	18.76	68.40	55.5	0.58
3	10.65	5.64	7.00	22.00	87.36	27.56	31.55	18.34	76.06	57.9	0.65
4	9.90	5.46	9.00	22.50	81.70	27.57	33.75	22.96	74.75	59.3	0.63
5	10.50	5.51	8.75	20.00	87.36	38.06	43.00	19.04	76.66	57.2	0.57
BEERS											
1	2.97	4.66	10.75	16.75	60.52	17.50	28.92	16.52	63.60	32.49	0.58
2	2.74	4.52	11.00	16.25	57.96	22.31	38.49	17.92	63.50	34.30	0.57
3	2.67	4.44	13.25	16.25	62.16	17.06	27.44	15.40	76.49	37.84	0.42
4	2.80	4.40	12.50	16.50	66.08	15.75	23.84	19.60	69.37	39.54	0.52
5	3.13	4.43	14.25	16.00	68.88	19.25	27.95	20.12	72.43	43.19	0.47

Acidity—(1) Titrated to neutral red.
(2) Titrated to phenol-phthalein.

Differences in the beers emphasise the importance of suitable liquor for beers of Pilsen type. The carbonate liquor, No. 1, gave the darkest beer, with a reddish tinge and a harsh, unpleasant bitterness. The softened water and softened water to which gypsum was added, Nos. 3 and 4, gave beers of a fine pale colour. The bitter of No. 3 was pronounced but pleasant. No. 4, though much superior to No. 1, clearly showed the disadvantage of gypsum, being harder and less pleasant than No. 3. The colours of Nos. 2 and 5 were the palest, with tendency to a greenish tint. Both beers were soft and rather lacking in hop flavour but it was judged that this could be adjusted by increasing the hop rate. Experience with these brews and others indicated that it is preferable to add lactic acid in the copper, rather than to the water. It then has the advantage of improving the copper break and decreasing the p_H of the beer without altering the composition of the wort.

These brews showed that the best liquor treatment for beer

of Pilsen type on the triple decoction system under the conditions existing at the particular brewery, with a water containing a considerable quantity of calcium carbonate, is softening with lime. As the nature of the malt and the process of brewing have an important influence on the result, it does not necessarily follow that this is the case in all circumstances. In some cases it is possible that softening, followed by addition of gypsum in quantity equivalent to the carbonate left, may give better results. In others acid treatment or addition of KHSO_4 may be found advantageous and, in an exceptional case, Lüers found that the best beer was obtained with an untreated hard water. In the particular case quoted the malt was of excellent quality, with rather high acidity and not suitable for use with soft water. This approximates to the conditions in an English top fermentation brewery, where the hard liquors are preferred for pale ales. The best method of treatment must, in fact, be dictated by the character of the raw materials and brewing conditions and can only be arrived at with certainty by actual trial.

(364) Treatment by Combination of Softening and Acid Addition.

The following example of treatment of a brewery liquor by a combination of softening and sulphuric acid addition was given by T. Hajek, Table 144. On account of the large quantity of $\text{Mg}(\text{HCO}_3)_2$ originally present, it was necessary to use the "split" softening process. Excess of lime was first added to the bulk of the water and afterwards neutralised by adding more of the raw liquor. The softened water was then treated with sulphuric acid. In the following analyses of the original and treated liquors there is an apparent increase of sodium. This was ascribed to sodium originally combined as silicate or with humic acid. The greater part of the silica was removed by the treatment.

TABLE 144.—TREATMENT BY SOFTENING AND ADDITION OF SULPHURIC ACID

Raw water Parts per 100,000				Treated liquor Parts per 100,000			
NaCl	2.57	NaCl	2.53
Na_2CO_3	5.19	Na_2SO_4	12.86
MgCO_3	27.78	MgSO_4	2.90
CaCO_3	33.78	CaSO_4	2.61
SiO_2	7.05	SiO_2	1.80
			<u>76.37</u>				<u>22.70</u>

(365) Liquor for Lager Beer of Munich Type.

Liquor composition is of less importance for beer of Munich type than it is for Pilsener. Nevertheless a water comparatively rich in calcium carbonate, such as is used in Munich, Table 123, Section 329, is most desirable. The typical rich aromatic flavour is not obtained with very soft waters, even though suitable malt is employed. Lüers suggested the hardening of soft waters by addition of bicarbonate solutions prepared in the following manner. Sufficient finely powdered calcium and magnesium carbonate to make up the deficiencies are added to the raw water in a tank fitted with a stirrer and perforated pipe through which a stream of CO_2 is passed from a fermenting vessel. 2 to $2\frac{1}{2}$ hours is required for solution of the carbonates, the water becoming perfectly clear on standing.

TABLE 145.—LIQUOR TREATMENT FOR BEER OF MUNICH TYPE
(EXPERIMENTAL BREWS)

	Soft Liquor		Hardened Liquor	
	Wort	Beer	Wort	Beer
Total N. mgm. per 100 ml.	126.80	105.28	121.96	98.44
Formol N. as % of total N.	36.5	26.3	32.9	28.4
P_2O_5 total mgm. per 100 ml.	110.20	—	78.88	—
„ inorganic „ „	91.34	—	73.61	—
„ organic „ „	18.86	—	5.27	—
Ash	228.0	—	217.4	—
Alkalinity of ash	5.66	—	5.0	—
Maltose gr. per 100 ml.	6.97	—	7.09	—
Maltose : non-maltose	1 : 1.11	—	1 : 1.07	—
Maltose % of extract	47.31	—	48.16	—
Colour (Brand)	—	8.5	—	8.0
Buffering N/10 p_{H} 7.07–5.67	14.5	7.6	17.5	9.2
„ „ p_{H} 5.67–4.27	11.0	10.0	9.0	10.0
„ „ total per 100 ml.	25.5	17.6	26.5	19.2
„ „				

The effect of hardening the liquor on the composition of wort and beer is shown in Table 145, using a dark Bavarian malt. As was to be anticipated with a water which reduces acidity and thereby restricts enzymic action in the mash tun, the most notable effects of the hardening were increase of the p_{H} of the worts and beers and restriction of proteolytic action in the mash tun, as shown by reduction in the total and formol nitrogen in the wort with a correspondingly reduced assimilation of nitrogen during fermentation. The wort from the hardened liquor also contained less phosphoric acid, but there was little difference in the maltose

content, the break or final attenuations. The beer from the hardened liquor was better and approximated much more closely to Munich beer than that from the soft untreated water. The total hardness of the untreated water was 3.8° , the temporary hardness 1.7° (CaO parts per 100,000). The treated liquor had a carbonate hardness of 15.96 , containing CaO and MgO in the ratio $11 : 4$.

METHODS OF LIQUOR TREATMENT BASED ON p_H CONTROL

(366) Theoretical Basis of Treatment.

The theories of ionic dissociation have helped to place liquor treatment on a more scientific basis, but it must be admitted that our knowledge of the rationale of this part of the brewing process is far from complete. No full explanation can yet be given of the changes in beer character and flavour resulting from the presence of such salts as sodium chloride or calcium sulphate, and the results are still so far obscure and depend so largely on the nature of the materials and on the brewing process that the best treatment must be found by trial in every case and modified from time to time as the results with changing materials prove to be necessary.

An advance was made when Fernbach and Hubert found that neutralisation of the alkalinity of wort, which Fernbach had previously observed to have an alkaline reaction to methyl orange and an acid reaction to phenol-phthalein, on account of the presence of primary and secondary phosphates, had a favourable influence on both diastatic and proteolytic activity, and established the fact that secondary phosphates retard enzyme action while primary phosphates increase it. This provided the key to an explanation of some, at least, of the beneficial effects produced by gypsum in mashing liquors and of the unfavourable influence of carbonates, as worked out by Windisch and others and described in the preceding chapter. Development of the conception of hydrogen ion concentration has in many ways brought increased precision to the practice of liquor treatment. It has emphasised the fact that the treatment must be varied according to the nature of the materials and brewing methods, and that the spargeliquor must be treated as well as the mashing liquor. It has also provided a means for judging the results by determination of the hydrogen ion concentration of the worts produced.

(367) Neutralisation with Acid.

Addition of the necessary amount of sulphuric, hydrochloric or lactic acid provides the cheapest and simplest method for removing the carbonates, but the greatest care must be taken to avoid the addition of excess of acid and the process should not be considered unless facilities for constant control are available. It has been developed since information was gained on the effects of different ions in the liquor and results in the exchange of the anions of the acid used for those of the carbonates present in the original water. The control by colorimetric determination of the p_H of the treated liquor is simple and must never be omitted. Sulphuric acid merely changes the carbonates of the water to an equivalent quantity of sulphates and is thus theoretically and actually a very suitable and inoffensive reagent when used in proper manner and quantity, although the addition of acid, except in the form of biologically acidified wort or malt, is forbidden by law in Germany and certain other countries. Lactic acid is preferred by some brewers to sulphuric as more natural to wort, though it is not to water, but hydrochloric acid is not generally desirable. The equation,



represents the reaction with sulphuric acid and indicates that it is necessary to add 98 parts by weight of sulphuric acid, exactly to neutralise 100 parts by weight of calcium carbonate, or that 1 equivalent or millival of acid is required for each equivalent or millival of carbonate to be removed. These proportions must never on any account be exceeded, as even small excess of acid may so raise the hydrogen ion concentration of the mash as to restrict or inhibit saccharification.

A simple method for determining the amount of acid required is provided by titration of 100 ml. of the raw water by N/10 acid, using methyl orange as indicator. The number of ml. required for neutralisation indicates the maximum amount of acid permissible with 100 ml. of the water. Each ml. of N/10 acid represents 0.0049 gram of sulphuric acid or sufficient to neutralise 0.005 gram of CaCO_3 or 0.0042 gram of MgCO_3 . If 10 lb. (one Winchester) of pure concentrated sulphuric acid is diluted by being slowly poured into 5 barrels of water (180 Imperial gallons) in a wooden vessel, it will be reduced approximately to decinormal strength. Consequently one barrel of this diluted acid or 2 lb. of concentrated acid may be added to 100 barrels of raw water for each ml. of N/10 acid required in the original titration. As the actual strength of the diluted acid is likely to be rather under decinormal, a little CaCO_3 should still remain in the water but, for

safety, it is advisable to add not more than $\frac{3}{4}$ of the amount of acid indicated by the preliminary titration.

In many cases better results are obtained by bringing the p_H of the treated water down to 7 only, leaving about 10 parts per 100,000 of CaCO_3 in the liquor. Brom-thymol blue may be used as an indicator for this purpose instead of methyl orange, titrating to a bluish-green colour at p_H 7. The necessary amount of acid found in this way is then added to the raw water. After treatment and thorough mixing a careful test must be made by adding a few drops of brom-thymol blue to a test tube of the treated water. A blue colour would show that the amount of acid added was insufficient, a yellow colour that the acidification had been carried too far. The treated liquor should be boiled to get rid of CO_2 which may corrode tanks and mains and possibly interfere with mash tun conversion.

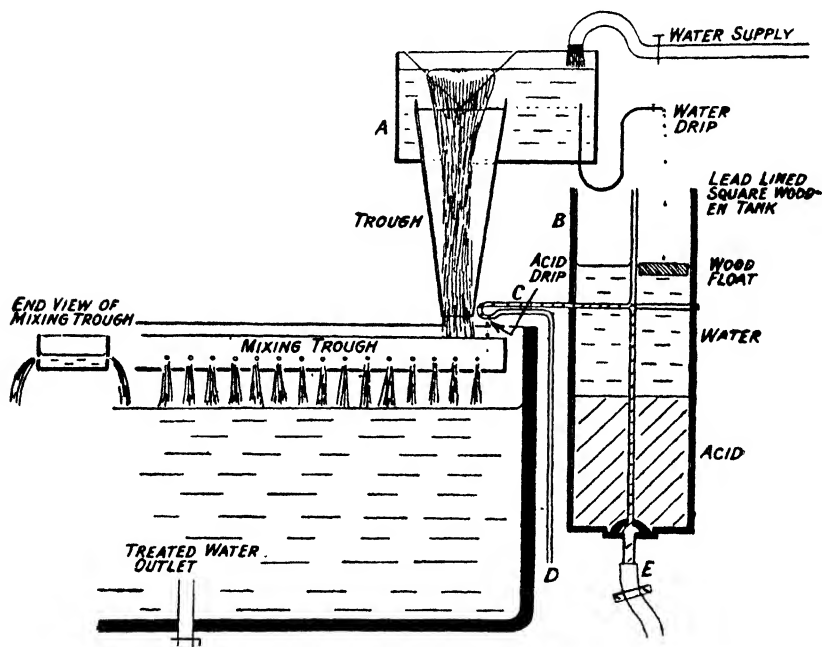


FIG. 63

AUTOMATIC PLANT FOR ACID TREATMENT

(368) Automatic Plant for Acid Treatment.

A continuously acting plant for addition of sulphuric acid has been described by McCandlish and Hagues³ and is illustrated in Fig. 68. The water is first passed into a feed box (A) in order to reduce fluctuations in rate of flow by passage through perforations in a sheet of metal which divides the box into two compartments.

In the end of the second compartment is a V-notch weir, over which the water flows in a constant stream into the mixing trough. A vertical narrow tube passes through the bottom of the second compartment and has its upper end slightly above the apex of the V-notch, so that when the water is flowing over the weir a proportionate trickle passes down the tube. The water drip is so arranged that it displaces an equal weight of acid from the acid container and this mixes with water which has passed over the weir. The acid container is a square wooden vessel (*B*) lined with lead. The water drip on to the float displaces acid upward through the acid drip pipe (*C*) into the mixing trough. The container is first charged with acid until the level of the latter is just below the horizontal part of the pipe (*C*) and then water is carefully added until the acid drip starts.

The acid drip hole is of such size as to permit normal drops to pass but when the hydrostatic equilibrium in the acid container becomes unstable through inflow of water and a sudden flow of acid with water takes place, the mixture runs past the acid drip hole in (*C*) into a carboy placed to receive it. The acid tank is then recharged. The capacity of the tank is one or two carboys of acid. The acid drip of the plant is adjusted in accordance with the nature of the water to be treated, so that, for example, 200 ml. of the treated water require about 4 ml. of N/10 acid to neutralise to methyl orange. This means that the water will have a p_H of about 7, the virage of methyl orange being at p_H 4.2. Frequent tests of the treated liquor must be made with bromthymol blue.

(369) Lactic Acid Treatment.

Neutralisation of the carbonates by means of lactic acid in place of sulphuric acid may have the same effect on the hydrogen ion concentration of the wort produced by the treated liquors with the same malt, but the salts produced are calcium and magnesium lactate in place of calcium and magnesium sulphate. This may in some cases be an advantage, in others a disadvantage. If it is desired to increase the SO_4 content of a liquor, then sulphuric acid is indicated as the most suitable reagent. The flavour produced by gypsum must, however, be taken into account. In any circumstances in which it is liable to affect the purity of flavour, lactic acid may be found preferable, as it is claimed to give a softer flavour in delicately hopped beers. The dissociation of the two acids must also be considered. While sulphuric acid is completely dissociated in dilute solutions, lactic acid is only dissociated to the extent of about 13% in N/100 solution. For

this reason an excess of lactic acid would not have the same harmful effect as the very slight excess of sulphuric acid which must always be guarded against. The increase of hydrogen ion concentration produced by slight excess of sulphuric acid has a very detrimental effect on enzymic conversion, while a considerably larger excess of lactic acid causes only a very small reduction in the p_H value of the mash. It has already been noted, in connection with liquor treatment for pale lager beers, that it may be preferable to add the lactic acid in the copper, rather than to the liquor.

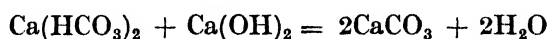
(370) Liquor Treatment with Lime and Acid.

The defects of the lime softening and acid treatments can be avoided by what in effect is a combination of the two, namely by the addition of lime followed by that of a small quantity of sulphuric acid or, preferably, acid potassium (or sodium) sulphate as suggested by Collett.⁴ Control of this process is based on correct adjustment of the hydrogen ion concentration of the treated liquor to that of the original water by means of the acid sulphate. Lime is added in quantity calculated as equivalent to the CO_2 present in the water. This usually brings the p_H value to between 8.5 and 9. If magnesium is present in the water, calcium chloride is added before the lime, slightly in excess of the quantity equivalent to the Mg, in order to promote complete precipitation of the carbonate as CaCO_3 . The precipitated carbonate can then be allowed to settle and the water drawn off into another tank, where sufficient acid potassium sulphate is added to neutralise the small quantity of hydroxides, convert some of the carbonates of magnesium and calcium remaining in solution to bicarbonates and bring the p_H value to about 7.3. Since, in most breweries, arrangements cannot be made for transferring the liquor from one tank to another, the acid potassium sulphate can be added previously to the settling of the calcium carbonate, in which case it is obvious that the carbonate cannot be reduced to such a low point as in the former method, but the p_H value of the treated liquor is readily restored to between 7.0 and 7.5. After the liquor has been softened in this way, gypsum or any other additions thought desirable can be made or, alternatively, they may be added before or during the softening process.

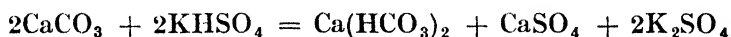
Softening with lime alone does not as a rule reduce the CO_2 content of the liquor below 4.0 parts per 100,000, but in the presence of calcium chloride it can be brought down to about 2.2 parts per 100,000, this figure closely representing the solubility of calcium carbonate in pure water. The carbonate remaining in the treated liquor is associated with both calcium and magnesium ions,

probably mainly the latter, in quantity represented by about 0.5 millival, but in the conventional method of expressing the hypothetical salts it will be shown as CaCO_3 .

The reaction with lime is represented by



With excess of calcium ions in solution, this reaction is fairly complete, Ca and CO_3 ions being removed until about 0.5 to 1.0 millival of each remains in solution, which is equivalent to 2.5 to 5.0 parts of CaCO_3 per 100,000. When the acid potassium sulphate is added in the same tank as the lime and calcium chloride, the further reduction of CO_3 is generally only very slight, the reaction is represented by the equation



The acid sulphate reacts, not only with the carbonate remaining in solution but, also, with some of the finer particles of carbonate precipitated by the lime. The solubility of the CaCO_3 and the evolved CO_2 both tend to keep the Ca and CO_3 ions constant at the above concentration. When the acid sulphate is added to the clear liquor, which has been allowed to settle in a separate tank, the further reduction of CO_3 ions is quite appreciable.

Examples of this method of treatment are given in the following Tables, of which the first represents the analyses of the untreated waters. In each case the required quantity of calcium chloride was first added, followed by the hydrated lime and finally by the acid potassium sulphate.

TABLE 146.—WATERS BEFORE LIME-ACID TREATMENT
(ANALYSES IN PARTS PER 100,000)

(A) Carbonate water, Lancashire				(B) Alkaline water, Middlesex			
Na ..	2·3	NaNO ₃ ..	2·6	Na ..	11·0	NaNO ₃ ..	0·8
Mg ..	0·7	NaCl ..	4·1	Mg ..	2·4	NaCl ..	11·7
Ca ..	12·0	MgSO ₄ ..	3·5	Ca ..	6·8	Na ₂ SO ₄ ..	17·0
NO ₃ ..	1·9	CaSO ₄ ..	6·8	NO ₃ ..	0·6	Na ₂ CO ₃ ..	1·6
Cl ..	2·5	CaCO ₃ ..	25·0	Cl ..	7·1	MgCO ₃ ..	8·4
SO ₄ ..	7·6			SO ₄ ..	11·5	CaCO ₃ ..	17·0
CO ₃ ..	15·0		<u>42·0</u>	CO ₃ ..	17·1		<u>56·5</u>
	<i>p_H</i> 7·5				<i>p_H</i> 7·8		

TABLE 147.—WATERS AFTER LIME-ACID TREATMENT
(PARTS PER 100,000)

(A) Carbonate water				(B) Alkaline water			
K	..	1.6	KNO ₃ .. 3.1	K	..	1.6	KNO ₃ .. 1.0
Na	..	2.3	KCl .. 0.8	Na	..	11.0	KCl .. 2.3
Mg	..	0.7	NaCl .. 5.8	Mg	..	2.4	NaCl .. 23.4
Ca	..	5.2	MgCl ₂ .. 0.9	Ca	..	2.0	Na ₂ SO ₄ .. 5.6
			MgSO ₄ .. 2.5				MgSO ₄ .. 12.0
NO ₃	..	1.9	CaSO ₄ .. 13.5	NO ₃	..	0.6	CaSO ₄ .. 2.8
Cl	..	4.6	CaCO ₃ .. 3.0	Cl	..	15.3	CaCO ₃ .. 3.0
SO ₄	..	11.5		SO ₄	..	15.4	
CO ₃	..	1.8		CO ₃	..	1.8	
			<u>29.6</u>				<u>50.1</u>
			<u><u>29.6</u></u>				<u><u>50.1</u></u>
			<i>p_H</i> 7.3				<i>p_H</i> 7.3

The first step in the treatment of (A) is addition of calcium chloride slightly in excess of the quantity equivalent to the magnesium found in the analysis, together with lime equivalent to the carbonate found. The quantity of CaCl₂ is found by multiplying the Mg by $\frac{55.5}{12}$ and the quantity of Ca(OH)₂ by multiplying the CO₃ by $\frac{37}{30}$, 55.5, 12, 37 and 30 being the equivalent weights of CaCl₂, Mg, Ca(OH)₂ and CO₃ respectively. The results are the necessary additions of CaCl₂ and Ca(OH)₂ in parts per 100,000 or grains per gallon, according as the analysis was expressed in one or other of these units. The actual quantities of the additions per 100 barrels may then be computed from Table 141. In the examples they are :

$$(A) \text{ CaCl}_2 \frac{0.7 \times 55.5}{12} = 3.24 \text{ parts per 100,000, or 2 pints CaCl}_2 \text{ solution per 100 barrels (3.5 parts per 100,000).}$$

$$\text{Ca(OH)}_2 \frac{15.0 \times 37}{30} = 18.5 \text{ parts per 100,000 or 7.3 lb. per 100 barrels.}$$

$$(B) \text{ CaCl}_2 \frac{2.8 \times 55.5}{12} = 12.9 \text{ parts per 100,000 or 7.4 pints per 100 barrels.}$$

$$\text{Ca(OH)}_2 \frac{17.1 \times 37}{30} = 21.1 \text{ parts per 100,000 or 8.3 lb. per 100 barrels.}$$

Allowance has been made in the treatment of (B) for an additional quantity of CaCl₂, equivalent to the sodium hypothetically combined as carbonate, 0.8 parts Na per 100,000. The total

quantity of CaCl_2 required by alkaline waters is found by adding half the sodium present as carbonate to the magnesium and calculating as for magnesium alone. It is equivalent to the difference between the millivals of CO_3 and Ca shown in the analysis, Table 148.

The final addition in each case was 2 lb. of KHSO_4 per 100 barrels, which served to adjust the p_{H} values to 7.3. The composition of the treated waters then became that shown in Table 147.

The treatments may be readily computed from the millinormality of the raw liquors, which is given in terms of millivals in Table 148, which serves as an example of the simplicity of liquor treatment from analyses expressed in this manner.

TABLE 148.—LIME-ACID TREATMENT OF WATERS
(CALCULATED ON MILLIVAL COMPOSITION)

(A) Carbonate water, Lancashire			(B) Alkaline water, Middlesex		
Millivals or N/1000			Millivals or N/1000		
	Untreated	Treated		Untreated	Treated
K'	—	0.4	K'	—	0.4
Na'	1.0	1.0	Na'	4.8	4.8
Mg''	0.6	0.6	Mg''	2.0	2.0
Ca''	6.0	2.6	Ca''	3.4	1.0
NO_3'	0.3	0.3	NO_3'	0.1	0.1
Cl'	0.7	1.3	Cl'	2.0	4.3
SO_4''	1.6	2.4	SO_4''	2.4	3.2
CO_3''	5.0	0.6	CO_3''	5.7	0.6

The treatments required can be immediately read off from the analysis of the raw waters when expressed in this way, and the necessary quantities of salts calculated or computed from Table 141. Thus the Lancashire water required 0.6 mval. or 3.33 parts per 100,000 of CaCl_2 to balance the 0.6 mval. of Mg, and 5 mvals. or 18.5 parts per 100,000 of $\text{Ca}(\text{OH})_2$ to react with the 5.0 mvals. of CO_3 or its equivalent of HCO_3 .

The addition of 0.6 mval. CaCl_2 adds 0.6 mval. of Cl and 0.6 mval. of Ca to the liquor, increasing the Ca to 6.6 mvals. The addition of 5 mvals. of $\text{Ca}(\text{OH})_2$ precipitates 4 equivalents of CaCO_3 , leaving 1 equivalent which approaches the solubility of CaCO_3 in water, thereby reducing the Ca to 2.6 mvals, and the CO_3 to 1 mval.

The CaCl_2 required for the alkaline water (*B*) is calculated from the difference between the ions of CO_3 and Ca , that is 2.3 millivals or 12.8 parts per 100,000. 5.7 millivals or 21.1 parts per 100,000 of $\text{Ca}(\text{OH})_2$ are then added.

Commercial acid potassium sulphate is not a compound of definite composition and the quantity required to adjust the p_{H} must be found by trial. The calculations given here are based on a product containing 30% free H_2SO_4 , 2 lb. per 100 barrels adding 1.6 parts per 100,000 of K and 3.9 parts of SO_4 , that is 0.4 mval. of K and 0.8 mval. of SO_4 .

The Lancashire water (*A*) treated in this way becomes of suitable composition for brewing mild or light bitter ales and can readily be hardened with gypsum for pale ales or more chlorine can be added in the form of potassium, sodium and calcium chlorides for mild ales.

The alkaline water from Middlesex cannot be converted into a very suitable liquor for pale ales, as the chlorides are unduly high, but it could be used satisfactorily for full mild ales and might be improved by adding calcium chloride in quantity equivalent to the sodium sulphate, that is 0.8 mval. or 4.44 parts per 100,000 CaCl_2 , and possibly a little gypsum. The treatment has been effective in reducing the carbonate ratio from 100 : 106 to 100 : 20.

The effect of the lime-acid treatment on the p_{H} of the water and wort and on the extract and colour obtained from an English malt is given in Table 149. Lime was added in amounts calculated to remove 25, 50, 75 and 100% of the carbonates, no allowance being made for the presence of free CO_2 which would prevent removal of the expected quantity of carbonates. Varying additions of calcium chloride were then made to keep the specific gravities of the waters constant, and the requisite quantity of acid potassium sulphate to neutralise the residual alkalinity of the 100% treated water was added in three cases.

TABLE 149.—EFFECT OF LIME-ACID TREATMENT ON p_{H} AND EXTRACT

Ca(OH) ₂ added pts. per 100,000	Mashing liquor				Wort				
	p_{H}	CO_3 pts. per 100,000	Sp. gr.	Ext.	Sp. gr.	Ext.	Cor- rected extract	p_{H}	Colour
No addition	8.08	14.4	1000.74	2.49	1028.71	96.74	93.98	6.37	5.5
4.41 + CaCl_2	7.64	11.7	1000.72	2.43	1028.97	97.34	94.91	6.07	5.0
8.82 + CaCl_2	7.64	9.0	1000.74	2.49	1029.05	97.61	95.12	6.02	5.5
8.82 + CaCl_2 + KHSO_4 ..	7.40	9.0	1000.72	2.43	1029.11	97.82	95.39	5.97	5.0
13.23 + CaCl_2 + KHSO_4 ..	7.57	7.5	1000.76	2.56	1029.35	98.62	98.06	5.91	5.0
17.63 + CaCl_2 + KHSO_4 ..	7.10	3.96	1000.76	2.56	1029.73	99.90	97.34	5.61	5.5

(371) A Test for the Effect of Liquor on Wort p_H .

An idea of the effect which a water will have on the p_H of the mash can be gained by titrating a mixture of the water and a suitable solution of buffer salts, as suggested by Lüers.⁵ One of Sørensen's buffer solutions giving a p_H of 5.91 and approximating in phosphate composition to the proportions of primary and secondary phosphates in worts can be used. It is made up from N/15 solutions of primary and secondary sodium phosphates (8 gr. NaH_2PO_4 in 1 litre and 9.467 gr. Na_2HPO_4 in 1 litre). The primary and secondary phosphate solutions are mixed in the proportion of 9 : 1 to give a buffer solution with a p_H value of 5.91.

15 ml. of the buffer solution is mixed with 75 ml. of the water, boiled for 5 minutes, cooled and made up to 100 ml. A control is made up with the same volume of buffer and distilled water. 20 ml. of each of the prepared solutions are titrated (a) with N/10 NaOH to phenol-phthalein and (b) with N/10 HCl to methyl orange. As an example, Lüers gave figures for the titration with a carbonate water from Munich and with the same water to which gypsum had been added, Table 150. These show that the reaction with the carbonate water is shifted considerably towards the alkaline side and that by the addition of gypsum the resulting reaction has been brought back towards that of the original buffer solution by an amount which is a measure of the effect of the treatment.

TABLE 150.—TITRATION OF BUFFERED WATERS

Titration with	15 ml. buffer, p_H 5.91, with 75 ml. water		
	Distilled	Munich	Treated
N/10 NaOH to phenol-phthalein ..	9.6 ml.	7.0 ml.	8.25 ml.
N/10 HCl to methyl orange ..	1.2 ml.	4.0 ml.	1.0 ml.

(372) Control of Liquor Treatment.

It must be emphasised that no hard and fast rules can be given for liquor treatment for any particular type of beer. So many variations are introduced by the character of the malt and other materials used and by the conditions of mashing, boiling and fermentation that each particular case must be dealt with individually, guided by the principles outlined and their application to the type of beer desired. The final decision can only be made after trials in the brewery in question, and any treatment decided upon must be reconsidered from time to time, as the materials or

other conditions are varied. This applies particularly to differences in malts due to seasonal effects.

In so far as liquor treatment is intended to supply the ions necessary to increase the hydrogen ion concentration of the mash or wort by reacting with malt constituents, or to remove those ions which reduce the acidity, its success may be measured by determination of the p_H of the wort. At present it is impossible to suggest any other practical methods of control, although it appears certain that some liquor constituents act otherwise than by regulating the reaction of the mash. The total effect can only be followed by the most careful scrutiny of the influence of different treatments on the character of the beer and such properties as flavour, brilliance and stability must be particularly noted. This can be assisted by analyses that throw light on the nitrogenous, carbohydrate and phosphate composition of the wort and beer and its buffering capacity. Indications have already been given of the value of p_H determinations on the liquor itself, but these are of limited utility as waters of very different composition may have a p_H value approximating to 7 and small differences may or may not be significant.

Since the hydrogen ion concentration of the mash depends to a considerable extent on the primary and secondary phosphates of the malt and the buffering power of various nitrogenous derivatives, while it is also influenced by the presence of organic acids and their salts, the quantity of salts added to the liquor must be governed in large measure by the quantities of these substances with which they will react or which are produced during mashing. That is to say the quantity of salts to be added for any particular type of beer will generally be greater as the specific gravity of the worts increases. The correct proportions for different materials or beers of varying strength may be ascertained from the p_H of the resulting worts. As a rule this should be in the neighbourhood of p_H 5.1 to 5.2 for ales, this value representing a near approach to the optimum for the diastatic, proteolytic and phospholytic enzymes. A p_H value of 5.4 or 5.6 is very generally considered satisfactory for all malt lager beers, but a p_H of 5.1 or 5.2 is probably preferable when malt adjuncts are used.

(373) Treatment of Sparge Liquor.

It is essential that the sparge liquor should be treated correctly as well as that used for the mash, since rise in the p_H value of the worts during the later runnings, when the lack of buffers derived from the malt permits of a marked increase in alkalinity, results in extraction and peptisation of colloidal nitrogenous substances

from the grains which will interfere with the clarification of the beer and its ultimate stability. Satisfactory conditions are attained when the p_H value of the worts remains practically constant, at about 5.2 for ales, throughout the whole period of sparging. If the carbonates in the liquor exceed some 6 or 7 parts per 100,000 a rise in the p_H value of the runnings commonly occurs at an early stage of sparging and, in bad cases, may increase to 6 or 6.5. When the liquor has been successfully treated, no greater rise than about 0.2 in p_H units should occur. For these reasons it is necessary that the capacity of the liquor tanks should be sufficient to permit of treatment of all the liquor used for mashing and sparging. Control by determination of the p_H value of worts at different periods of the running off is particularly valuable during sparging.

(374) Summary.

Liquor treatment is intended to adjust the composition of the available water supply to that most suitable for brewing the type of beer desired. It should produce a liquor which will :

- (1) Ensure that the p_H value of the mash is most advantageous,
- (2) Yield wort of the composition and p_H value best adapted to coagulation of the proteins and fermentation.
- (3) Have most beneficial effects on the flavour of the beer.
- (4) In some, but probably rare, cases add salts required for yeast nutrition.

The requirements in respect of wort composition and flavour vary in different types of beer, with different materials and brewing conditions. The best guide under these circumstances has been the composition of typical natural brewing waters and, until recently, liquor treatment has been based on imitation of these waters by removal of redundant salts or addition of those lacking.

The predominant salts in brewing liquors are usually carbonates of calcium and magnesium and sulphates of calcium and magnesium. It is usually necessary to remove a proportion of the carbonates as they displace the p_H value of the mash further from the optimum for enzyme action. Calcium sulphate tends to increase the acidity of the mash and its addition is advantageous for many types of beer, but not for all. A moderately hard carbonate liquor is best for dark, full-flavoured beers and a very soft water for pale lager beers. Gypseous liquor is considered most suitable for pale and bitter ales.

The salts of sodium are generally undesirable if in excess, but additions of sodium and calcium chloride are frequently made to increase the fulness of mild ales and stouts.

The most commonly employed methods of treatment are :

(1) Softening by boiling or by addition of lime, for pale lager beers.

(2) Softening, followed by addition of gypsum, for other lager beers and ales.

(3) Addition of comparatively large quantities of gypsum and other salts, for ales.

(4) Neutralisation of part of the carbonates by sulphuric acid, for ales and lager.

(5) Combination of lime softening and acid treatment, KHSO_4 being used in place of sulphuric acid, for ales and lagers.

The control of liquor treatment depends on determination of the p_{H} value of the wort. Its success must be judged by the flavour and other properties of the beer, and by the behaviour of the wort throughout the brewing process.

It is essential that the sparge liquor should be treated in such a way that the p_{H} value of the later worts from the mash tun does not materially increase.

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NAME INDEX

References are to numbered sections, not to pages.

- ALDOUS, A. G., Parker, A., Tosswill, C. G.,
Walker, T. K., 257
Anderson, J. A., 37
Adler, L., 162
Arrhenius, S., 92
- BAKER, J. L., 127
Baker, J. L., and Hulton, H. F. E., 128,
177, 219, 231
Baker, J. L., and Ward, T. J., 53
Beaven, E. S., 10, 16, 17, 19, 20, 21, 43, 46
Bishop, L. R., 56, 60, 66, 68, 69, 73, 74, 76,
145, 152, 153, 205
Bishop, L. R., and Day, F. E., 73, 74
Bishop, L. R., and Marx, D., 71
Bjerrum, J., 99, 115
Bronchley, W. E., 14, 15
Briant, L., 235
Briant, L., and Meacham, C. S., 274
Brown, A. J., 15, 45
Brown, A. J., and Clubb, D., 270
Brown, A. J., and Ward, G. B., 270
Brown, H. T., 7, 10, 42, 43, 58, 63, 141, 150,
170, 284
Brown, H. T., and Escombe, F., 15
Brown, H. T., and Glendinning, T. A., 122
Brown, H. T., Morris, G. H., and Millar,
J. H., 236, 241, 247
Buchner, E., 8, 119
Bungener, A., 268
Bungener, A., and Lintner, C. J., 268
Burgess, A. H., 255, 257
- CAGNIARD DE LA TOUR, C., 6
Chapman, A. C., 270, 279, 284
Chrzaszcz, T., 138
Chrzaszcz, T., and Janicki, J., 138
Coleman, D. A., and Snider, S. R., 172
Collett, J. H., 370
Comrie, A. A. D., 62
Cosbie, A. J. C., 255
Crowther, E. M., 62
- DIXON, T. R., 216
Dubrunfaut, A. P., 119
- EASTCOTT, E. V., 62
Elford, W. J., and Ferry, J. D., 85
Engledow, F. L., 19
Escombe, F., 42
- FERNBACH, A., and Hubert, H., 97, 335, 366
Fernbach, A., and Stoleru, I., 272
Fink, H., 56, 149, 266, 285
Fink, H., and Hartman, F., 149
Fink, H., and Kunisch, G., 68
Fischer, E., 109, 119
- Fletcher, L., and Westwood, J. B., 142
Ford, J. S., 270
Ford, J. S., and Guthrie, J. M., 137, 142
Ford, J. S., and Tait, A., 274, 278
- GAY-LUSSAC, J. L., 7
Geys, K., 56
Goldiner, F., and Klemann, H., 242
Graham, T., 79
Guthrie, J. M., and Philip, G. G. A., 276
- HAJEK, T., 364
Hansen, E. C., 7
Hagues, G., 340
Harden, A., and Young, W. J., 124
Harlan, H. V., 17, 31
Harlan, H. V., and Florell, V. H., 32
Harlan, H. V., and Mann, A., 15
Harlan, H. V., and Martini, M. L., 30
Harrington, G. T., 70
Hartong, B. D., 56, 164, 186
Hastings, J. J. H., Pyman, F. L., and
Walker, T. K., 270
Hastings, J. J. H., and Walker, T. K., 278
Hawley, L. F., and Norman, A. G., 110
Haworth, W. N., 106, 109
Haworth, W. N., Hirst, E. L., Kitchen, H.,
and Peat, S., 107
Hayduck, F., 268
Heron, H., 307
Hind, H. L., 142, 154, 199
Hind, H. L., and Beettlestone, N. C., 333
Hind, H. L., and Hammett, E. N., 187, 188,
192
Hind, H. L., and Lancaster, H. M., 176, 185
Hind, H. L., Threadgold, H., and Arnold,
M. D., 177
Hirst, E. L., Plant, M. M. T., and Wilkin
son, M. D., 106
Hjalmar-Nilsson, N., 26
Hofman-Bang, G., 68, 69, 70, 157
Hofmeister, E., 89
Hopkins, R. H., 132
Hopkins, R. H., and Burns, J. A., 131, 228
Hopkins, R. H., Cope, G. F., and Green,
J. W., 123, 137
Hopkins, R. H., Hind, H. L., and Day,
F. E., 178
Hopkins, R. H., and Kelly, H. E., 162, 340
Höppler, E., 183
Huber, I., 255
Hulton, H. F. E., and Ward, T. J., 212
Hunter, H., 22
- JARY, S. G., 263
- KJELDAHL, T., 117, 122, 178

NAME INDEX

References are to numbered sections, not to pages.

- Kolbach, P., 102, 187, 190, 273
 Kolbach, P., and Antelmann, H., 161
 Kolbach, P., and Kleber, W., 274
 Kolbach, P., and Schild, E., 147, 158, 214
 Kolbach, P., and Simon, H., 142
 Kühne, W., 119
 Kützing, F., 6
 Krause, B., 242
- LANE, J. H. and Eynon, L., 247
 Laufer, S., 143
 Lavoisier, A. L., 6
 Leberle, H., 62
 Leeuwenhoek, A. von, 6
 Liebig, J. von, 4, 5, 6, 7
 Lindet, L., 58
 Ling, A. R., 106, 220
 Ling, A. R., and Nanji, D. R., 106
 Lintner, C. J., 58, 122, 142, 274
 Loeb, J., 114
 Lott, F. E., 319, 324
 Lüers, H., 56, 162, 363, 365, 371
 Lüers, H., and Geiger, O., 154
 Lüers, H., and Loibl, H., 149
 Lüers, H., and Malsch, L., 128, 132, 134
 Lüers, H., and Nishimura, N., 148, 342
 Lüers, H., and Volkamer, W., 144
 Lundin, H., 26
- MANN, A., and Harlan, H. V., 15, 46
 Maillard, L. C., 209
 Maquenne, L., and Roux, E., 106
 Mason, F. A., 52, 53
 McCandlish, D., and Hagues, G., 368
 Miller, T. S., 70
 Moritz, E. R., and Morris, G. H., 62
 Moufang, E., 56, 131, 333
 Munro, J. M. H. and Beaven, E. S., 42, 43, 72
 Myrbäck, K. and S., 136, 142
- NANJI, H. R., and Norman, A. G., 58
 Nilsson-Ehle, H., 26
- OHLSSON, E., 137, 162
 Oliver, J. H., 205
 Osborne, T. B., 60
 Osborne, T. B., and Campbell, G. F., 111, 152
 O'Sullivan, C., 58, 247
 Ostwald, W., 82
- PASTEUR, L., 6, 7, 8, 119
 Payen, A., and Persoz, 5, 119
 Piratzky, W., 153, 166, 183
 Piratzky, W., and Rehberg, R., 151, 157
 Piratzky, W., and Wiecha, G., 144, 183
 Preece, I. A., 110
 Pringsheim, H., 124
 Prior, E., 62, 160
- REHBERG, R., 165
 Richardson, W. A., Higginbotham, R. S., and Farrow, F. D., 106, 107
 Risler, J., 279
- Rose, R. C., and Anderson, J., 68, 153
 Russell, E. J., and Bishop, L. R., 61
- SALAMON, A. G., and Goldie, E. N., 235
 Salmon, E. S., 258, 261, 292, 295, 298, 303
 Salmon, E. S., and Amos, A., 252
 Salmon, E. S., and Ware, W. M., 259
 Samec, M., 106
 Sato, M., 131
 Schild, E., 155
 Schjerning, H., 152, 157, 187
 Schmidt, J., Winge, O., and Jensen, J. P. H., 308
 Schönfeld, F., 159
 Schryver, S. B., and Thomas, E. M., 106
 Schwann, T., 6
 Sedlmeyer, J., 163
 Shimwell, J. L., 176, 267, 272
 Shimwell, J. L., and Kirkpatrick, W. F., 270
 Siau, R. L., 354
 Siau, R. L., and Hodson, A. R., 147
 Siegfried, H., 335
 Siller, R., 273
 Sörensen, S. P. L., 95, 114
 Svedberg, The, 111
- THÉNARD, L. J., 6
 Thunaeus, H., and Schröderheim, J., 156
 Tombeur, F., and De Clerck, J., 302
 Turpin, W., 6
- VALENTINE, G., 212
 Van Laer, M. H., 162
 Van Slyke, D. D., 98, 115
- WAHL, R., and Henius, M., 64
 Waldschmidt-Leitz, E., and Mayer, J., 137
 Waldschmidt-Leitz, E., and Purr, A., 131, 137
 Waldschmidt-Leitz, E., Reichel, M., and Purr, A., 137
 Walker, T. K., 273, 275, 305
 Walker, T. K., and Hastings, J. J. H., 254, 274, 277, 302, 305
 Walker, T. K., Hastings, J. J. H. and Aldous, A. G., 257.
 Walker, T. K., Hastings, J. J. H., and Farrar, E. J., 271
 Walker, T. K., and Parker, A., 271, 273
 Wiebe, G. A., 13, 33
 Wieland, H., 268
 Wiggans, R. G., 17
 Willstätter, R., 119
 Windisch, W., 70, 336
 Windisch, W. and F., 345
 Windisch, W., and Kolbach, P., 177
 Windisch, W., Kolbach, P., and Schleicher, R., 273
 Windisch, W., Kolbach, P., and Schüren, W., 275
 Windisch, W., Kolbach, P., and Vogl, C., 187
 Wöllmer, W., 268, 274, 275, 302
 Wright, G. S., 148

SUBJECT INDEX

References are to numbered sections, not to pages.

ACETAMIDE, 112
 Acetate buffer, 97
Acetobacter, 267
 Acidity, 93, **95**, **96**, 103
 Activators, **124**, 127, 137
 [a]_D 177, **244-246**
 Adsorption, **84**, 85, 91, **132**, 137, 269
Aerobacter aerogenes, 314
 Albumin, 80, 81, **111**, 116, 117, **152**
 Albumose, 113
 Aldohexose, 105, 109
 Aleurone, 14, 15
 Amides, 112, 113
 Amino-acids, 112, **113**, **114**, **155**
 Amino index, 113
 Ampholytes, 87, **99**, 115
 Amylase, **127**, **137**, **138**
 Amylo-amylase, 106
 α-amylodextrin, 107, 109, 127
 Amylo-kinase, 124, 127, 137
 Amylopectin, 106
 Amylo-phosphatase, 137
 Amylose, 106
 Anions, anode, 92
 Araban, arabinose, 105, 110
 Asparaginase, 125
 Asparagine, 112, 152
 Asymmetric carbon, 109

BACILLUS cereus, 270
coli, 314
Bacterium C and X, 270
 Balling, **242**
Barley, 9-77
 Abyssinian, 17
 acidity, 62
 Algerian, 17, 38
 American, 28-**30**, 32, 34, **35**, **39**
 analysis, **55**, 74, 75
 Anatolian, 27
 Archer, 19, 21, 22
 Argentino, 17
 ash, **62**
 Atlas, 13, 33, 45
 Australian, 27, 36, 38
 autumn sown, 23
 B 244, 19
 Bahari, 38
 Bavaria, 25
 Bay Brewing, 17, 33
 Beardless, 32
 Beere, 19
 Benghazi, 38
 Beyrout, 17
 Bigg, 19
 Binder, 21, 22, 26, 37, 69, 70

Barley—*continued*.
 Bohemian, 25
 Brage, 26
 Brewing Californian, 17
 British, 17, **19-24**
 Burton Malting, 21
 bushel weight, 22
 Californian, 13, 17, 27, **33**, **34**, **36**
 Canadian, **37**, 68
 carbohydrates, 55-57, 58, **71**
 cell walls, 15, 144
 Chevallier, 17, 19, 22, 26, 27
 Chilean, 17, 27, 38
 classification, 13, 16, **17**, 28
 Club Mariout, 17, 34
 Coast, 13, 17, 33
 colour, 13, 17, **45**
 composition, 55-77
 corn, **12**, **14**, **15**
 Cyprus, 38
 Czechoslovakian, **25**
 damaged, **48**
 Danish, 26, 27
 Danubia, 25
 Danubian, 17
 density, 11, 17
 development, **14**
 diastase, 127, 137
 districts, **23**
 drying, **50**, **70**
 Duckbill, 37
 ear, **10**, 17
 Egyptian, 38
 embryo, 12, 14, 15
 endosperm, 12, 15
 English, 17, **19-24**
 enzymes, 15, 126-137
 Escourgeon, 17
 extract, 73-76
 F 112, 17, 19
 Fan, 17
 fat, 163
 fertilisation, 14
 fertilisers, 61
 fertility, 17
 flower, 10, 14
 Forty-fold, 22
 four-rowed, 11
 French, 26
 fungoid diseases, **52**
 Gabes, 38
 Gaza, 17, 38
 germination, **49**
 German, **25**
 Glabron, 32
 glumes, 14
 Gold, 22, 26

SUBJECT INDEX

References are to numbered sections, not to pages.

Barley—continued.

Golden Archer, 22
 Golden Pheasant, 21
 Goldthorpe, 17, 19, 21, 23
 grading, **35, 51, 63, 64**
 gums, **58, 144**
 Hallett's Pedigree, 19
 Hanna, **25, 27**
 Hannchen, 26, 27, 37
 heated, 48
 hemicelluloses, **55, 58**
 Hero, 32, 34
 historical, 9
 hooded, 13, 14
 Horn, 27
 Horsford, 32
 husk, 13, 14, **44, 55, 56**
 huskless, 13, 14, 16
 hybrid, 13, 20
 identification, **13**
 immature, 42, 69
 Indian, 38
 insect pests, **53**
 Invincible, 21
 Isaria, 24–26
 judging, 41–53
 July, 17
 Kenia, 24, 26
 Kent, 23
 Kinver, 19
 lemma, 13, 14
 Lincoln, 23
 Lion, 32
 lodging, 23
 lodicules, 14
 Machiné, 38
 Maja, 26
 malting quality, **41, 63, 76**
 Manchuria, 17, **28, 30, 31, 68**
 Manshury, 31
 manure, 61
 Mariout, 34
 maturation, **42, 61, 69, 70**
 mealy, **43**
 Mediterranean, **28, 30**
 Mexican, 17
 microscopical structure, **15**
 Minnesota, 31
 moisture, 50, 55
 Moravian, 25
 Morocco, 17
 mow burn, 48
 naked, 13, 14, 16
 narrow-eared, 10, **11, 16, 17, 22, 39, 46**
 New Cross, 22
 nitrogen, 20–22, 24, 43, 55, **59–61, 63, 64, 66, 68–74, 76, 150–158**
 Norfolk, 23
 O.A.C.21, 17, 31, 37
 Odessa, 31
 Opal, 22, 26
 Ouchak, 17, 27, 45
 palea, 13, 14
 Palestine, 38
 Peacock, 17
 pectins, **58**

Barley—continued.

pericarp, 15
 phosphates, 62
 physical characters, 41–48
 physiological characters, 41–53
 Plumage, 21–23
 Plumage-Archer, 9, 17, 20, **21, 23, 37, 56, 66, 68**
 Polish, 26
 prediction extract, **74, 192**
 Prentice, 26
 Prior's Chevallier, 19, 27
 Princess, 22, 26
 protein, **55, 59–61, 63, 64, 66, 68–70, 72–74, 150–158**
 quality, 41–54, **63, 64**
 quarter, 22
 races, **16, 17**
 rachilla, 13
 regularity, physical, **47**
 composition, **66, 67, 71, 72**
 ripeness, 14, **42, 61, 69**
 Scandinavian, **26**
 Scotch, 23
 scutellum, 15, 46
 sea mist, 23
 season, 24, 51, 61
 selection, 20
 semi-permeable membrane, 14, 15
 shape, 46
 silica, 62
 six-rowed, 11, 13, 16, 17, 19, **29, 38, 46, 68**
 size, 46
 Slovakian, 25
 smooth-awned, **32**
 Smyrna, 17, 38
 soil, 24, 61
 Somerset, 23
 Spanish, 17, 38
 Spartan, 27, 32
 species, **16, 17**
 Spratt, 19, 22, 23
 Spratt-Archer, 17, 20, **22, 23, 51**
 standards, **36, 37**
 Standwell, 21, 23, 68
 starch, 15, 55, **57**
 steely, 42, 43, 70
 steeping loss, 56
 storage, **70**
 structure, **15, 46**
 Success, 32
 Suffolk, 23
 Svalof, 25, 26
 Swedish, 26
 Syrian, 27
 specific gravity, 181
 Tennessee Winter, 33
 testa, 15
 Thorpe, 37
 thousand-corn weight, 38, 73, 74
 Trebi, 31, 37
 Tripoli, 17, 38
 Tunis, 17, 38
 types, 23, 27, 39, 40
 valuation, 41–53
 valve, valvule, 13, 14

SUBJECT INDEX

References are to numbered sections, not to pages.

Barley—continued.

varietal characters, **24, 68, 71, 76, 156**
 constant, **73, 74**
 Vaughn, **32, 34**
 Velvet, **32**
 Victory, **26**
 weevils, **53**
 White Smyrna, **27**
 wide-eared, **17, 21**
 winter, **19**
 Winter Club, **17**
 Wisconsin, **32, 37, 38**
 Yerli, **17, 38**
 Yorkshire, **23**
Balling, 242
Baumé, 242
Beet sugar, 231
Bios, 160
Boozah, 9
 Bordeaux mixture, **259**
 Brand colour scale, **174, 178**
 Break, **89, 116, 352**
 Brewers' pounds, **2, 239**
Brix, 242
 Bubbles, **86**
 Buffers, **97, 98, 102, 162, 335-337, 338, 342, 344**
 Buffer titration, **98**
 Bynin, **152**

CALGON, 359
 Calomel electrode, **100**
 Candy, **231**
 Cane sugar, **108, 109, 231**
Caramel, 235
 malt, **214**
 Carbohydrases, **125**
 Carbohydrates, **55-57, 58, 71, 105-110, 145-149**
 Catalase, **136**
 Catalysts, **120**
 Cataphoresis, **87**
 Cathode, cation, **92**
 Cellulosan, **110**
 Cellulose, **55, 58, 105-107**
 Cereals, **221-228**
 Chancellor ale, **1**
 Chlorophyll, **104**
 Clerget, **246**
 Coagulation, **88, 89, 91, 116, 187, 339**
 Coefficient of modification, **188**
 Coenzymes, **124**
 Cold water extract, **147, 175, 186**
Coli-aerogenes, **314**
 College ale, **1**
Colloids, 78-91, 183
 definition, **81**
 electrical phenomena, **87**
 lyophilic and lyophobic, **88, 89**
 properties of, **83-86**
 protection, **90**
 size of particles, **80**
 systems, **82**
 Complement, **124**
 Congress analysis, **170, 173, 178**
 Continuous phase, **82**
 Copper sugars, **234**

Cozymase, **124**
 Crystalloids, **79**
 Crystal malt, **214**
 Cupric reducing power, **109, 247**
 Cytase, **128, 144**

DECARBOXYLASE, 125
 Degrees, gravity, **237-242**
 Denaturation, **116**
 Density, **237**
 Desamidase, **125, 136**
 Desmo-enzymes, **121**
 Desmolases, **125, 136**
 Dextrin, **90, 105, 107, 124**
 Dextrin-maltose, **233**
 Dextrinogenamylase, **137**
 Dextrinolytic activity, **142**
 Diastase, **119, 122, 124, 125, 127, 137, 138, 142, 266**
 Diastatic activity, Lintner, **177, 178**
 Pollak-Egloffstein, **178**
 Windisch-Kolbach, **177, 178**
 Dipeptidase, **131**
 Disaccharides, **105, 109**
 Dispersion, **82**
 Dissociation constant, **94**
 ionic, **92**
 Downy mildew, **259**

EDESTIN, 157
 Electrolytes, **92**
 Electron, **92**
 Eleuto-amylase, **138**
 Emulsoids, **82**
 Energy, surface-, **83**
Enzymes, 119-139
 activators, **124**
 activity, **122**
 adsorption, **132, 137**
 amylases, **127, 137, 138**
 amylo-phosphatase, **137**
 bacterial, **127**
 carbohydrases, **125**
 catalase, **135**
 catalysts, **120**
 conditions of activity, **123, 205**
 cytase, **128**
 decarboxylase, **125**
 desamidases, **125**
 desmolases, **125**
 diastase, **119, 122, 124, 125, 127, 137, 138, 142, 266**
 eleuto-amylase, **138**
 endo- and extra-cellular, **121**
 function of, **126**
 inhibitors, **124**
 invertase, **130**
 isolation, **132**
 lipase, **134**
 and liquor, **343**
 malt, **126-139**
 maltase, **129**
 nature, **119**
 nomenclature, **125**
 optimal conditions, **123**
 oxidases, **125**
 oxido-reductases, **125**

SUBJECT INDEX

References are to numbered sections, not to pages.

Enzymes—continued.

- papain, 133, 137
- pepsin, 131, 133, 137
- peptidase, 131, 132
- peroxidase, 125
- p_n , 123, 343
- phosphatases, 134
- and phosphates, 335, 343
- phytase, 134
- proteolytic, 120, 124, 125, 131, 132, 133, 137
- proteolytic, insoluble, 142
- purification, 132
- saccharogenamylase, 137
- sisto-amylase, 138
- soluble and insoluble, 121
- sucrease, 125
- synthesis by, 126
- tryptase, 131
- Equivalent weight, 92, 318
- Escherichia coli*, 314
- Extract, 240, 242**
 - barley, 75
 - index, 192
 - malt, 146, 147, 173, 185, 205
 - prediction, 74, 192

FEHLING'S solution, 247

- Fermentation, 3, 109
- Ferments, 5, 119
- Filtration, 85
- Finings, 90
- Flakes, 226–228
- Flavobacterium proteus*, 267
- Flocculation, 89, 116, 339
- Foams, 86
- Formol nitrogen, 114, 155, 156
- Fructose, 105, 108, 109
- Fulness of flavour, 183
- Fungicides, 84

GALLON, 317

- Gelatin, 87, 90, 115
- Gels, 82
- Gibbs and Thomson's Law, 86
- Glass electrode, 100
- Globulin, 111
- Glucose, 105–108, 109, 129, 233, 241
- Glucuronic acid, 109
- Glutelin, 111, 153
- Glycine, 99, 112
- Grain, unmalted, 221–228
- Grains, 56, 110, 173, 335
- Gram's stain, 267
- Gravity, 237–242
- Grits, 224, 225, 227, 228
- Gum, 86, 90, 105, 110
- Gypsum, 89, 116, 310, 325, 326, 333–340, 342, 343

HAZE, 183

- Hemicellulose, 105, 110, 128, 144, 149
- Hexosans, 105, 107
- Hexoses, 105, 109
- Hofmeister series, 89
- Hops, 250–308**
 - Amos' Early Bird, 289

Hops—continued.

- analysis, biological, 270, 271, 277, 278
- colorimetric, 276
- gravimetric, 274
- Log phase, 271
- validity, 278
- antiseptics, 267–278, 303–306
- influence of p_n , 272, 275
- value, 270
- aphis, 263
- aroma, 254, 279, 280, 301, 302
- arsenic in, 307
- Auscha, 295
- Australian, 300
- bales, ballots, 256
- Belgian, 297
- bine, 251
- bitter acids, 268, 269
- bitterness, 302, 308
- black blight, 263
- bracts, bracteoles, 252
- Bramling, 289, 293, 303
- Brewer's Favourite, 292, 303
- Gold, 292, 303
- browing liquor, 298, 302, 339
- brewing value, 301–308
- British Columbian, 299
- brush, 252
- burr, 252
- Butcher system, 253
- Buvrinnes, 297
- canker, 261
- Canterbury Golding, 289, 303
- certificated, 256
- chlorotic disease, 262
- Czechoslovakian, 295
- climate, 253
- Cobb, 290
- cold packed, 255, 302
- cold storage, 257
- Colegate, 291
- colour, 254
- cone, 252
- condition, 252
- constituents, 266
- contamination, 307
- Continental, 294–297
- copper in, 259, 307
- Cross Butcher, 253
- cultivation, 253
- cuttings, 251
- diastase, 266
- diseases, 258–262
- Downy mildew, 253, 254, 259
- dry, 280, 306
- drying, 255, 302
- East Malling, 292, 303
- eelworm, 262
- English, 288–293, 303, 304
- enzymes, 257
- extracts, 282
- Farnham, 289
- fertilisation, 251
- Fillpocket, 292
- fire blight, 264
- flavour, 302, 303, 339
- flower, 251, 252

SUBJECT INDEX

References are to numbered sections, not to pages.

Hops—continued.

fly, 263
Fuggle's, 251, 253, 259, 262, **291**
French, **297**
German, 256, **294**
Goldings, 288, **289**
Golding varieties, 288, **290**
grades, 277, **304**
growing, **253**
Hallertau, 294
hand examination, 301
hanging, 254
heated, 301
Hersbruck, 294
humulon, **268**, 273-275, **302**
insect pests, 263, 264
leaf spot, 261
lice, 263
lupulin, 252, 257
lupulon, **268**, 273-275, **302**
male, 251, 252, 260
marking, **256**
Mathon, 289, 293, **303**
microflora, 257
moisture, 255, 266
mosaic, 258, 262
mould, 252, 254, **260**
nettlehead, 262
new varieties, **292**
New York, 298
New Zealand, **300**
nitrogen, **284**
oil, **279-281**
old, 257
Oregon Cluster, 298, 302, **303**
Oregon Fuggle, 298
Pacific Coast, 293, **303**
packing, **256**
pectins, **285**
Petham, 303
physical examination, 301
picking, 254
plant, **251**
pockets, 256
pole and wirework, 253
Polish, **296**
pollination, 252
preservative substances, 266-278
preservative value, 254 255, 257, **275**
303-306
Prolifics, 287, 291
Quality Hop, 292
red spider, **284**
reek, 255, 302
resins, 266-278, 301-306
 analysis, 274-278
 drying temperature, 255
 fractionation, **273**
 hard, 255, 273, 302
 properties, 267-269, 302
 soft, 255, 273-275, 302
 storage, 257
ripeness, **254**
Rodmersham, 289
Saaz, 295, 297, 301-303
seed, 252
selection, 308

Hops—continued.

sets, 251
soil, 253
Sonomas, 298, 303
Spalt, 294
storage, **257**
Styrian, 296, 302-303
sulphur, 255, 294
tannin, **283**
Tettang, 294, 297
Tolhursts, 288, 291
Tutsham, 290, 293, **303**
umbrella system, 253
valuation, 301-307
virus diseases, **262**
weather, 254, 301
wilt, 261
wireworm, 263
Worcester System, 253
yearlings, 302
yeasts on, 266
Yugoslavian, **296**
Hordein, 111, 112, **154**
Humulon, **268**, 273, 275
Humulene, 279
Hydrocyanic acid, 124, 133
Hydrogen ions, 92-103
 determination, 100, 102
 enzymes, 123, **333**, **334**
 mash and wort, **334-337**, 339
Hydroxonium ions, 93
Hydrometers, 237, 238

INDICATORS, 101
Inositol, 105
International sugar scale, 245
Invertase, 109, **130**
Invert sugar, 105-108, 109, **232**
Ionic activity, 93
 concentration, 92
 dissociation, 92, 94, 115
Ions, **92-96**, **317-320**, **337**
Iron, 283, 310, 315, 318, **337**
 bacteria, 315
Isinglass, 90
Isoclectric point, 87, 89, 99, 115, 116

KAINITE, 361
Ketoheose, 105, 109
Khapra, **53**
Kjeldahl's law of proportionality, 122

LACTIC acid, 161, 216, 363, 369
Lactobacillus bulgaricus, 271
 delbrückii, 270
 pastorianus, 267
Lactose, 105, 108, 109, **230**
Lambic, 222
Leucine, 112
Leucosin, 152
Lignin, 58
Linhart kiln, 255
Linseed, 90
Lintner value, 142
Lipase, **135**
Lupulin, 252, 257, 279
Lupulon, **268**, 273, 275, **302**
Lyoenzymes, 121

INDEX

References are to numbered sections, not to pages.

Lyophilic colloids, 82, **89**, 90
 Lyophobic colloids, 82, **88**
 Lyotropic series, 89, 90

McConkey, 314

Maize, **221-228**

oil, 223

Malt, 140-220

acidity, **161**

amber, **213**

analysis, 167-178, 215

interpretation, 180-207

standard, **17Q**

American, **202**

aroma, **210**

ash, **159**, 335, 336, 340

black, **212**

Bohemian, 198

brewing value, **180-184**

brown, **213**

buffers, **162**

Californian, **200**

Mariout, 201

cane sugar, 1-8

caramel, **214**

Chilean, 201

Chevallier, 198

classification, **206**

coefficient of modification, 188-190

cold water extract, **147, 175, 186**

colloids, **183**

colour, **174, 210**

coloured, 211-214

analysis, 215

Congress analysis, **170, 178, 204**

crystal, **214**

cytase, **144**

Danish, 203

defective, **197**

Diamber, **217**

diastase, **142, 177**

Dixon's Enzymic, **216**

Egyptian, 201

English mild ale, **196**

pale ale, **195**

six-rowed, **199**

Enzymic, **216**

extract, **173**

coarse and fine, **185**

index, 192

prediction, 192

fat, **163**

forced, **176**

foreign two-rowed, **198**

six-rowed, **200-202**

grades, **180**

hemicelluloses, **149**

hordein, **154**

husks, **165**

index of modification, 188-190

lager, American, **202**

European, **203-204**

Lintner value, 142, 177

mineral matter, 159-162

modification, **141, 180-190, 203**

analysis, 184-188

and brewing value, **182**

Malt—*continued*.

modification—

coefficient of, **188-190**

physical, **181**

moisture, **172**

mould, 168

Munich, 203

nitrogen content, **151, 187-191**

migration, **150**

permanently soluble, 155-158, **187,**

188, 190, 191

P.S.N. value, **187, 188, 190**

wort, 206

oat, 219

phosphates, **160; 334-336, 340**

physical characters, **167, 168, 180, 181**

Pilsen, **203**

proteins, **152-155, 187**

proteolysis on kiln, **158**

proteolytic enzymes, **143**

regularity, 168

roasted, **211**

rye, 219

saccharification, 177

sampling, **171**

selection, **205, 206**

sinkers, **181**

six-rowed, **39, 140, 153, 188, 192**

199-202

specific gravity, 181

starch, **146**

Syrian, 201

tannin, **164**

types, **167**

unsoundness, 168

valuation, 180-188

wheat, **218**

yeast nutrients, **191, 206**

Malt adjuncts, **221-235**

Malt extract, **220**

Maltase, **129**

Malting, 140-166

aeration, 157

biochemistry, **104**

chemical changes, **145-165**

CO₂ effects, 157

enzymic changes, **142-144**

germination, **157**

kilning, 147-148, **158**

loss, 151

respiration, 151

Maltose, 105, 108, 109

Mannose, 105, 109

Mash phosphates, **335, 336, 343**

reaction, **334, 336**

Masscuite, 236

Melanoidins, **209**

Melibiose, 105, 109

Meta-proteins, 112

Metric units, 236

Micelles, 82, 84

Micrococcus, 267

Microscopic vision, 80

Millilitre, 236

Millival, 318

Modification, **141, 182-190**

coefficient, **188**

SUBJECT INDEX

References are to numbered sections, not to pages.

- Modification, index, 188
 Mohr's cc., 236
 Mosaic, 262
 Muta-rotation, 109, 246
 Myrcene, 279
- NETTLEHEAD**, 262
 Nitrates, nitrites, 312, 350
Nitrogen, amide, 117
 amino (*see* formol)
 barley, 20-22, 24, 43, 57, 59, 61, 63, 64,
 86, 68-74, 76
 coagulable, 116, 117
 enzymes, 131-133
 formol, 113-114, 155, 156, 187
 hops, 284
 malt, 150-158, 184, 187-193
 permanently soluble, 155-158, 187-191
 phospho-tungstic and phospho-molybdic,
 117
 tannin, 117
 water, 350
 wort, 117
 Normality, 92, 93, 96; 318
- OATS**, 219
 Optical activity, 108, 109, 244-246
 Original gravity, 243
 Oryzenin, 222
 Osazones, 109
 Osmotic pressure, 79
 Oxidases, 125
 Oxido-reductases, 125
- PAPAIN**, 131, 133, 137
 Pasteurisation, 91
 Pectins, 58, 105, 183, 285
 Peeterman, 222
 Pentosans, pentoses, 105, 110
 Pepsin, 131, 137
 Peptidase, 132
 Peptide linkage, 112
 Peptides, 112, 113
 Peptisation, 82
 Permutit, 351
 Peroxidase, 125
- P_H**, 92-99
 acidity scale, 96
 buffers, 97-99
 determination, 100-102
 enzymes, 123, 343
 hop antiseptics, 272
 hop flavour, 302, 339
 hydrogen ion concentration, 95
 indicators, 101
 liquor treatment, 363, 366-373
 mash reaction, 333-338
 proteins, 115-116
 water, 322, 342
 Phosphatases, 134
 Phosphates, 160, 333-337, 340
 Phosphoric acid, 98
 Phytase phytin, 134
 Plato tables, 242
 Polarimetry, 244
 Polar groups, 86
 Polypeptides, 113
 Polysaccharides, 105, 106, 109
 Polyuronides, 110
 Prediction equations, 74, 192
 Primings, 230, 234, 241
 Protease, 131
 Protection, 90
Proteins, barley, 55, 59-70, 72-74
 breakdown products, 113, 114, 155-158,
 182, 184, 187, 190
 coagulation, 116
 colloids, 79, 80, 87-89, 115
 constitution, 111
 hydrolysis, 112
 malt, 150-154, 189
 modification, 182, 184, 187, 188, 190,
 191
 physical properties, 115
 rest, 333
 Proteolysis, 150-158, 333, 334
 Proteolytic enzymes, 131-133, 143
 Protozoa, 313
 Pounds, Brewers', 2, 239
- QUEEN'S College Brewery**, 1
- RAFFINOSE**, 105, 109
 Raw grain, 221-228
 Raw sugar, 230-231
 Reaction of medium, 103
 Red spider, 264
 Reducing power, 105, 106, 108, 109, 247
 Refined grits, 225
 Refractometer, 243
 Resins, 266-278
 Rice, 222, 223, 224, 226, 227, 228
 Rye, 219
- SACCHARIFYING diastase**, 142
 Saccharimeters, 245
 Saccharogenamylase, 137
 Saccharometers, 238
 Salting out, 89, 112
 Sampling, 171
 Semi-permeable membrane, 115
 Sensitisation, 90
 Sinker test, 168
 Sisto-amylase, 138
 Soap solution, 86, 321
 Sols, 82-89
 Soluble starch, 107
 Solution, 79
 divisor, 175, 241
 Sørensen titration, 114
 Sparging, 127, 344, 373
 Specific gravity, 237
 rotation, 177, 244-246
 Starch, 106, 146
 sugars, 233
 Standard analyses, 170, 178
 Stereoisomerism, 109
 Stewing on kiln, 147
 Substrate, 122
 Sucrase, 130
 Sucrose, 105, 108, 109, 231
Sugars, 105, 108, 109
 analysis, 236, 248
 brewing, 230-248

SUBJECT INDEX

References are to numbered sections, not to pages.

Sugars—continued.

- beet, 231
- candy, 231
- cane, 105, 108, 109, **231**
- caramel, **235**
- dextrin-maltose, 233
- fructose, 105, 108, 109
- glucose, 105, 108, 109, 129, **233**, 241
- invert, 105, 108, 109, **232**
- lactose, 105, 108, 109
- maltose, 105, 108, 109
- mannose, 105, 109
- melibiose, 105, 109
- optical activity, 108, 109, **244** **246**
- primings, **230-234**, 241
- raffinose, 105, 109
- raw, 230, 231
- reducing power, 105, 106, 108, 109, **247**
- solution divisors, 175, **241**
- starch, **233**
- Sulphate ions, 89
- Sulphur dioxide, 255
- Superclastase, 127
- Surface activity, **83**, 86
- tension, 83, 86
- Suspensoids, 81

- TAKA-DIASTASE, 137
- Tannin, **164**, **283**
- Tanno-peptones, 283
- Tintometer, 170, 174, 178
- Trihexosan, 107
- Trisaccharides, 105, 109
- Tryptase, 131
- Tyndall effect, 80, 115

- ULTRA-MICROSCOPY, 80
- Uronic acids, 109, 110
- Urono-araban, 110
- Urono-xylan, 110

- VAN SLYKE analysis, 114
- Ventzke scale, 244
- Viscosity of wort, 144

WATER, 309-374

- ales, for, 340, **360**, **361**
- acid treatment, 363, **364**, **367-369**
- acidity effects, **333** **338**, 342-345, 347
- alkaline, 330, 333, **352**, **362**
- salts, **345**, 347
- aluminium, 318
- ammonia, 312
- analysis, 311, 312, 317-319
- anions, 318, 320
- bacteria, 311, 313, **314**, 315
- beer character, 309, 310, **339** **346**
- bicarbonates, **338**
- bottle rinsing, 314
- buffers, 335, 337, 338, 340, **342**
- Burton, 310, 319, **324**, **325**, 360
- Burtonizing, 362
- brewing types, **323**
- calcium carbonate, 310, 320, 321, 338
- chloride, 360, 361
- phosphates, 335-337
- salts, 336, 337, 346
- sulphate, 310, 311, **334-340**, 360, 361

Water—continued.

- carbonate ratio, 323, **347**
- carbonates, 310, 314, 320, 321, 335-339, 341, 345, 360-373
- carbonic acid, 322
- cations, 318, 320
- chalk, 328, 329
- chlorine, 311, 312, 345, 360
- Clark degrees, 321
- coli-aerogenes*, 314
- contamination, **311-314**
- decarbonation, **355**, **356**
- deuterium, 316
- diplogen, 316
- dissolved substances, **310**
- Dortmund, **326**
- Dublin, **329**, 360
- Edinburgh, **327**
- electro-osmose, **358**
- enzymes, **343**
- flavour of beer, **339**, 345
- gases in, 310
- gypsum, 310, 325, 326, **334-340**, 360, 361
- hard, 309, 310, 321
- heavy, 316
- hop flavour, 339
- ions, **94**, 310, 317-320, 322, 323, **337**
- iron, 310, **315**, 318, 331
- bacteria, **315**
- Kainite, 361
- lactic acid, 363, **369**
- lager, 326, 329, 331, 332, **362**, **365**
- London, **328**, **330**, 362
- McConkey, 314
- magnesium salts, 310, 329, 335-337, **341**, 342, 346, 360
- manganesec, 315
- mash reaction, **334-336**, 343
- metals, heavy, 316
- microscopical examination, **313**
- mild ales, 328, 332, 361
- millivials, **318**
- moorland, 314, 331
- Munich, **329**
- natural, 310
- nitrate, 312, 328, 345, **350**
- nitrites, 312, 345
- odour, 314
- organic matter, 312
- oxygen absorbed, 312
- pale ale, 310, 325, 332, 360, 361
- pathogenic bacteria, 314
- pH*, **94**, **322**
- peaty, 315, 348
- phosphate reactions, **335-337**, **343**
- physiological effects, **346**
- Pilsen, 331
- potassium, 318, 345
- quantity required, 309
- radio-activity, 316
- rain, 310
- rare elements, 316
- saline, 310, **349**
- constituents, **320**
- salt effects, **333-338**
- sand filters, 313
- silica, 318

SUBJECT INDEX

References are to numbered sections, not to pages.

Water—*continued*.

sodium carbonate, 336, 337, **352**
chloride, 345, 346, **349**
nitrate, 345, **350**
sulphate, 345, **351**
soft, 309, 315, 321, 363
softening, **354-359**
sparge, **344, 373**
stout, 328-330, 332, 360
supplies, **309**
surface, 313, 322
treatment, **360-373**
acid, 364, **367-369**
for ales, **360, 362**
control, **371, 372**
empirical, **360**
for lager, **363 365**
lime-acid, **364, 370**
types, **332**
weather effects, 311
wort effects on, **333 346**

Weiss beer, 218

Wheat malt, **218**

Wort ash, 335

break, 89, 116, 352

buffers, 335-337, 338, **342, 344**

nitrogen, 206

phosphates, **335-343**

reaction, **334-345**

solids, 205

XYLAN xylose, 105, 110

YEAST in hops, 266

nature of, **6**

and nitrates, 345

nutrition, **191**, 196, 200

surface coatings, 84

ZEIN, 222

Zwitterions, 99, 115

Zymase, 121, 125

